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SYNTHETIC RESIN ADSORBENTS IN TREATMENT OF INDUSTRIAL WASTE STREAMS

by

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16. ABSTRACT

The use of synthetic polymeric adsorbents for removal of organic pollutants from industrial waste streams is a viable alternative to more common treatment methods such as carbon adsorption. However, resin technology is not widely practiced due to the difficulty of selecting the appropriate synthetic adsorbent/regenerant combination for a particular application. This research program was undertaken to develop a simple, reliable laboratory test to assess the feasibility of using synthetic resin adsorbents for treatment of a given waste water stream.

The new test method facilitates rapid screening of a large number of adsorbent/regnerant pairs. The test consists of exposing small bags of adsorbents in the actual waste stream for predetermined periods of time, followed by regenerating the exposed adsorbents. The batch portion of the test measures regenerated saturation capacity of any adsorbent/regenerant pair with a single analysis. The rate portion measures regenerated capacity as a function of time.

Capacity data obtained by the test method were compared and correlated with data obtained by conventional isotherm tests and column experiments. In general, the batch test performs better than the isotherm test in predicting column saturation capacity of polymeric adsorbents.

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FOREWORD

The Environmental Protection Agency is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise, and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life. In partial response to these mandates, the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, is charged with the mission to manage research programs to investigate the nature, transport, fate, and management of pollutants in ground water and to develop and demonstrate technologies for treating wastewaters with soils and other natural systems for controlling pollution from irrigated crop and animal production agricultural activities; for developing and demonstrating cost-effective land treatment systems for the environmentally safe disposal of solid and hazardous waste.

EPA, as provided for in the Clean Water Act, has the responsibility to promulgate regulations to protect streams. These regulations must be developed based on consideration of tehcnology for waste treatment. Synthetic resin adsorbents are known to be excellent for the treatment of specific organic pollutants. However, there has been no reliable, simple way to assess the practicality and cost of wastewater treatment with these adsorbents. This project has developed a test procedure which provides the equilibrium and kinetic data needed for the evaluation of the treatment of industrial wastewater by synthetic resin adsorbents. Thus, the comparison of the results of more conventional treatment options such as activated carbon or biological methods with resins is now possible.

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ABSTRACT

The use of synthetic polymeric adsorbents for removal of organic pollutants from industrial waste streams is a viable alternative to more common treatment methods such as carbon adsorption or steam stripping. However, resin technology is not widely practiced due to the difficulty of selecting the appropriate synthetic adsorbent/regenerant combination for a particular application. This research program was undertaken to develop a simple, reliable laboratory test to assess the feasibility of using synthetic resin adsorbents for treatment of a given waste water stream. Since a major advantage of resin technology is ease of resin regeneration and possible recovery of organic pollutants for recycle, the test was designed to measure regenerated adsorption capacities directly.

The new test method, the batch/rate test, facilitates rapid screening of a large number of adsorbent/regenerant pairs. The test consists of exposing small bags of adsorbents in the actual waste stream for predetermined periods of time, followed by regenerating the exposed adsorbents. The batch portion of the test measures regenerated saturation (equilibrium) capacity of any adsorbent/regenerant pair with a single analysis. The rate portion measures regenerated capacity as a function of time.

Adsorbents used for the test development included several Rohm and Haas resins, several Mitsubishi resins, and several Calgon activated carbons. Adsorbent performance was evaluated in several single component synthetic streams, a multicomponent synthetic stream, and a multicomponent real stream. These streams contained one or more of the following organic pollutants: toluene, nitrobenzene, 2-nitrophenol, 2,4-dinitrotoluene, tetrachloroethylene, 1,2-dichloropropane. Regenerants evaluated included acetone, methanol, and/or steam.

Capacity data obtained by the batch/rate test method were compared and correlated with data obtained by conventional isotherm tests and column loading/regeneration experiments. In general, the batch test performs better than the isotherm test in predicting column saturation capacity of polymeric adsorbents. Because the test method is designed to measure solvent regenerated capacity, it is not suitable for evaluation of activated carbons which are usually regenerated in furnaces at very high temperatures. The batch/rate test provides the equilibrium and kinetic data needed to predict column performance under a variety of operating conditions. A simple theoretical model, developed for use with batch/rate data, satisfactorily predicts column performance to within 10% of experimental results during the first half of column breakthrough. Alternately, a simple empirical relationship between batch data and initial column breakthrough can be used to estimate initial leakage to within 15% of experimental results. Thus, with a single measurement, the batch test, column capacity to 10% leakage can be roughly estimated to be equal to 70% of the batch capacity.

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SECTION 1

INTRODUCTION

PURPOSE AND APPROACH

The objective of this project was to develop a simple, reliable laboratory test to assess the applicability of synthetic resin adsorbents for removal of organic pollutants from industrial waste streams. The test has been designated the batch/rate test. Since a major advantage of resin adsorption technology in waste water treatment is ease of resin regeneration and possible recovery of pollutant materials, the test was designed to measure regenerated adsorption capacities directly. The test consists of exposing small bags of adsorbents in a waste stream for predetermined periods of time followed by regenerating the exposed adsorbents to obtain regenerated capacities. Typical regenerants include organic solvents (e.g. methanol, ethanol, acetone, toluene), steam, and dilute caustic. Usually the choice of regenerant is determined by cost, safety factors, and process compatibility as well as success in regeneration. The batch portion of the test measures regenerated saturation (equilibrium) capacity for any adsorbent/regenerant pair with a single analysis. Batch capacity corresponds to maximum column saturation capacity. The rate portion of the test measures regenerated capacity as a function of exposure time in the waste stream. From the batch test alone, a large number of adsorbent/regenerant pairs can be rapidly evaluated to determine if any resins are worth additional testing in the waste stream. The optimum adsorbent/regenerant pair(s) can then be used in rate testing to generate the additional data needed to calculate column performance under a variety of column operating conditions. Treatment costs can then be estimated.

The adsorbents available for evaluation during batch/rate test develop ment included several Rohm and Haas Amberlite* and Ambersorb* adsorbents, several Mitsubishi Diaion** adsorbents, and several Calgon Filtrasorb*** granular activated carbons. During the initial stages of test development, adsorbent performance was evaluated in synthetic single component waste streams by standard isotherm tests, by column loading/regeneration experiments, and by batch/rate tests. After batch/rate test optimization, adsorbent performance was evaluated by batch/rate testing and column studies. Several more single component waste streams, a synthetic multi-component waste stream, and a real contaminated groundwater source were used.

* Amberlite and Ambersorb are registered trademarks of the Rohm and Haas Company.

** Diaion is a registered trademark of Mitsubishi Chemical Industries, Ltd.

*** Filtrasorb is a registered trademark of the Calgon Corporation.

ADSORPTION PHENOMENOM

A brief introduction to the factors which influence adsorption is presented here. More detailed information can be found in the literature[1-8].

The phenomenom of physical adsoprtion onto solids is due to electrostatic and covalent interactions between the sorbate and the solid surface. Many types of forces are involved including van der Waals forces, dipole-dipole interactions, and hydrogen and hydrophobic bonding. It is not possible to accurately predict which species will be adsorbed well by a given adsorbent. However, a useful adsorption concept is that hydrophobic or non-polar molecules or portions of molecules are attracted to hydrophobic surfaces, and that hydrophilic or polar molecules are attracted to hydrophilic surfaces. In adsorption of organics from aqueous streams, the portions of the organic molecules with less affinity for water, i.e. the hydrophobic portions, are preferentially adsorbed onto the hydrophobic surfaces of the adsorbent while the hydrophilic portions of the molecules remain oriented in the aqueous phase. Since synthetic adsorbents are available over a wide range of surface polarities, they have the potential for efficiently and selectively adsorbing many types of organic compounds.

The capacity of an adsorbent for an adsorbed species is highly influenced by its surface area and pore structure. In general, the greater the surface area, the greater the amount of adsorbate which can theoretically be adsorbed. However, the adsorbent's pore size range and distribution pattern must be sufficient to permit adsorbates to migrate through the pores to the adsorbing surfaces. Surface area and pore size are inversely related. Thus pores must be large enough to admit molecules to the adsorbent interior, yet as small as possible to maximize available surface areas. It is reasonable to expect that for treatment of a complex waste stream, several adsorbents of differing surface polarity, surface area, and pore structure might be needed to remove the organic contaminants from the aqueous stream.

A principal difference between synthetic resin adsorbents and granular activated carbons is the lower binding affinities of the resins for sorbates. Thus, resins can be readily regenerated *in situ* with organic solvent or steam whereas carbons are usually regenerated in furnaces at very high temperature (e.g. 800°C).

The adsorption of organic pollutants from aqueous streams is influenced by many factors other than the physical and chemical nature of the adsorbent. Some of the more important factors to be considered include the solubility, polarity, and concentration of the sorbate; the stream temperature and pH; the presence of competing sorbates; the type and concentration of dissolved electrolytes; and the quantity and size of suspended particulates. An increase in solubility, ionization, or temperature generally results in a decrease in adsorption.

Conversely, the presence of added electrolytes usually improves adsorption. However, the presence of competing organics to be adsorbed may enhance, interfere with, or act independently in the adsorption process. Since so many factors influence adsorption, extrapolation of capacity data obtained in either synthetic single component streams or in synthetic multicomponent streams may not accurately reflect adsorption of selected sorbates from a real waste stream.

SECTION 2

CONCLUSIONS

The experimental protocol developed for measuring the adsorptive capacity of synthetic resin adsorbents, i.e. the batch/rate test, provides a simple reliable procedure for assessing the practicality of using synthetic adsorbents for toxic waste water treatment. In resin applications, the test method is superior to conventional isotherm techniques developed for carbon adsorption because it provides a means of assessing resin regeneration as well as resin adsorptive capacity. The batch portion of the test measures regenerated saturation capacity and the rate portion measures regenerated capacity as a function of time. Using batch/rate data and a simple, theoretical performance model, resin column performance under a variety of operating conditions can be satisfactorily predicted during the first half of column breakthrough. Alternately, using a simple empirical relationship, initial column leakage can be approximated to within 15% of experimental results from batch data alone.

SECTION 3

RECOMMENDATIONS

The batch/rate test has been shown to be a rapid, reliable method of assessing the treatability of toxic waste streams with synthetic resin adsorbents. Although resin technology is a viable alternative to the more common treatment methods (e.g. activated carbon adsorption, liquid-liquid extraction, steam stripping or biological treatment), it is not widely used due to the difficulty of selecting the appropriate adsorbent/regenerant combination for a particular waste stream. Guidelines need to be established for choosing which of the numerous adsorbent/regenerant systems to evaluate in a specific application. Using the batch/rate test and its associated predictive models, the various commercially available resin adsorbents should be screened in a broad spectrum of industrial waste streams. The resulting data, along with other published adsorption data, should then be tabulated to provide a guide which correlates the type of waste stream or class of pollutant with the adsorbent/regenerant system(s) expected to be most successful in treatment.

SECTION 4

MATERIALS AND METHODS

ADSORBENT CONDITIONING AND HANDLING TECHNIQUES

Twelve adsorbents, including ten synthetic resins and two granular activated carbons, were used in this study. Table 1 is a list of selected physical properties of these adsorbents. The Mitsubishi and Rohm and Haas synthetic resins were conditioned with methanol and water prior to use as described in Appendix B. This preconditioning was done to remove the preservatives and residual monomers from the pores of these adsorbents.

Moisture content of each conditioned resin was determined by analytically weighing approximately 5 g of conditioned resin, drying the resin in a 110°C oven for 2 hours, and reweighing. For all experimental procedures, resins were weighed in their wet form and the weight was multiplied by % solids to determine the dry weight for calculations.

% Solids = (g dry resin/g wet resin) x 100

The granular activated carbons were used in their dry form without any pretreatment. In the carbon adsorption isotherm study by Dobbs and Cohen, the carbon was pulverized, screened, and slurried before use[9].

ANALYTICAL METHODS

Solutions were analyzed on a Hewlett Packard 5710A Gas Chromatograph equipped with a flame ionization detector for >5 ppm studies and an electron capture detector for <10 ppm studies. A 6' x 1/8" SS column of 60/80 mesh Tenax GC was used. The data were recorded and analyzed with either a Spectra Physics Autolab system IVB Integrator or a Hewlett Packard 3390A Reporting Integrator.

Solutions for immediate analysis were placed in 1.5 mL Wheaton vials filled to about 7/8 capacity, sealed with Teflon-lined serum caps, loaded onto a Hewlett Packard 7671A Auto Sampler, and analyzed. Solutions for later analysis were placed in vials filed to capacity (i.e., with no air space), sealed, and refrigerated. This method of sample handling and storage was particularly critical for aqueous solutions of the pollutants. Aqueous solutions in unsealed or improperly sealed vials decreased in concentration by as much as 25% in 8 hours. Each sample was analyzed in triplicate and if any value exceeded the average by >5%, the sample was reanalyzed. In comparing the data presented in this report, this ±5% error limit should be considered.

TABLE 1

PHYSICAL PROPERTIES OF ADSORBENTS

Adsorbent	Manufacturer	Chemical Nature	Pore Vol. (cm^3/g)	Surface Area(m^2/g)	Pore Dia. Ave. (Å)	Surface Polarity
Amberlite XAD-2	Rohm and Haas	polystyrene	0.68	300	100	low
Amberlite XAD-4	Rohm and Haas	polystyrene	0.96	725	50	low
Amberlite XAD-7	Rohm and Haas	acrylic ester	0.97	450	85	intermediate
Amberlite XAD-8	Rohm and Haas	acrylic ester	0.82	160	150	intermediate
Ambersorb XE-340	Rohm and Haas	polymer carbon	0.34	400	200,15[a]	very low
Ambersorb XE-347	Rohm and Haas	polymer carbon	0.41	350	200,5[a]	low
Ambersorb XE-348	Rohm and Haas	polymer carbon	0.58	500	200,15[a]	intermediate
Diaion HP-10	Mitsubishi	polystyrene	0.64	500	–[b]	low
Diaion HP-20	Mitsubishi	polystyrene	1.16	720	70	low
Diaion HP-30	Mitsubishi	polystyrene	0.87	570	–[b]	low
Filtrasorb 300	Calgon	activated carbon	0.85	1000	–[b]	intermediate
Filtrasorb 400	Calgon	activated carbon	0.94	1125	–[b]	intermediate

[a] Ave. pore diameter of the macropores and micropores, respectively.

[b] Ave. pore diameter not available.

Standard solutions for GC calibration were made by analytically weighing the pollutants and dissolving them volumetrically with purified water or the organic solvent which was used as the regenerant. Plots of GC area versus concentration were fitted by linear regression analysis to obtain the calibration curves. Organic solutions of very high concentration (e.g., >10,000 ppm) exhibited non-linear behavior. Such solutions were diluted volumetrically to fall within the linear calibration region.

PREPARATION OF SYNTHETIC WASTE STREAMS

A 25 x 600 mm column was filled to 2/3 height with Amberlite XAD-2 which had been treated with the organic(s) required in the synthetic waste stream. Resin loading was done approximately on a gram organic per gram resin basis. For example, 220 g resin in water was treated dropwise with stirring with 220 g organic. Solid organics were added as a slurry in acetone/water, methanol/water, or toluene/water as determined by the type of stream desired. The mixture was then placed in a jar and shaken on a platform shaker for about a week. The solution was decanted and the loaded resin was washed with several 200 mL portions of purified water. After the resin was slurried into the column, it was washed with 10 L of purified water.

The loaded column was connected via Teflon tubing and Teflon or stainless steel adapters to a large, stirred reservoir (e.g., 5 L, 4-neck flask) filled with a nearly saturated aqueous solution of the organic(s). The synthetic waste stream was continuously pumped through the column and recycled through the reservoir at a rate of ca. 5 BV/hr (50 mL/min). The solution contacted only glass, Teflon, or stainless steel. Nearly constant concentration waste stream was withdrawn as needed for the various tests, and make-up or dilute solution was added. After initial start-up, equilibration time for addition of 1 to 4 L of make-up solution was about 16 hours.

SECTION 5

ADSORPTION TEST METHODS

ADSORPTION ISOTHERMS

Adsorption isotherm tests were performed in Alltech 100 mL Reaction Vials. Four or five different weights of each adsorbent to be tested were added to separate vials. The following dosages are provided as a guide for performing these isotherm tests: 1) for initial pollutant concentrations of about 200 ppm use 0.04 to 0.5 g adsorbent, 2) for initial concentrations of about 2000 ppm use 0.2 to 1.7 g adsorbent. At low pollutant concentrations, carbonaceous adsorbents have higher capacities than polymeric adsorbents. Thus, lower dosages of carbonaceous adsorbents are required to achieve similar equilibrium concentrations. After addition of adsorbent, the vials were filled to capacity (about 120 mL) with the known concentration waste stream using a repipette dispenser. For the control experiment, an empty vial was similarly filled with the waste stream. The vials were sealed with Teflon-lined silicon rubber septa and aluminum crimp caps, and shaken on a platform shaker for a minimum of seven days until equilibrium was attained. The reaction vials were opened and supernatants were transferred to vials for GC analysis (vide supra). From the weight, volume, and concentration data, the adsorption capacity of each resin was calculated and plotted according to the Freundlich equation.

BATCH/RATE TESTS

The adsorption procedure of the batch/rate test was performed in the reservoir portion of the synthetic waste stream system. "Tea bags" formed from ca. 25 sq in pieces of Teflon macrofiltration material (mesh size 75 to 150 microns) and stainless steel wire were filled with 0.5 g (dry weight) adsorbent. The bags were suspended in the reservoir which was stirred rapidly at ~400 rpm. After a predetermined exposure time, the "tea bag" was dewatered by draining and blotting with filter paper and then stored in a tightly capped vial with minimum air space until regeneration was performed.

Regeneration was performed on the entire amount of adsorbent in an 8 mL mini-column. Twelve bed volumes of regenerant were pumped through the column at a rate of 6 BV/hr (~15 mL/hr) or, the adsorbent was steam treated for 2 hours. During adsorption and regeneration, solvents and solutions contacted only glass, stainless steel or Teflon. The regenerant solution was collected and its volume was measured. To determine the amount of eluted pollutant, a sample was placed in a vial and analyzed by GC (vide supra). The column containing regenerated adsorbent was dried at 110°C for 2 hours and the weight of dry adsorbent was obtained. The adsorbent's capacity in mg/g was then calculated: regenerant concentration (mg/L) x regenerant volume (L) ÷ adsorbent weight (g).

Batch Test

1. A "tea bag" containing ca. 0.5 g of each adsorbent to be tested was placed in the waste stream for a minimum of 48 hours. (Time sufficient for saturation of the adsorbent with pollutant is required).

2. After saturation, the adsorbent was dewatered (drained and blotted), transferred to a mini-column, and regenerated.

3. Adsorbent weight and solution volume and concentration were determined as described above.

4. The regenerated adsorption capacity at saturation was calculated for each adsorbent.

Rate Test

1. 5 to 7 "tea bags" containing ca. 0.5 g each of the same adsorbent (generally the best adsorbent) were placed in the waste stream.

2. The bags were removed at predetermined times over a 24-hour period. At least 4 samples were removed during the first hour. (If waste stream concentrations were much less than 100 ppm, these times were increased significantly).

3. The adsorbent from each bag was dewatered, placed in a separate mini-column, and regenerated with a known effective regenerant.

4. Adsorbent weight and solution volume and concentration were determined as previously described.

5. The regenerated adsorption capacity at each exposure time was calculated.

6. The "adsorption" rate was obtained from the slope of a graph (or linear regression analysis) of the adsorption capacity versus time during approximately the first hour, and the mass transfer coefficient was calculated.

COLUMN EXPERIMENTS

Column experiments were conducted in Ace 11 x 600 mm jacketed chromatographic columns fitted with Teflon adapters and removable glass filter discs. Weighed, conditioned adsorbent was slurried into a column and backwashed with high purity water to give 100% bed expansion for 30 minutes. The adsorbent was then allowed to settle prior to any down flow of water. This procedure classified the adsorbent bed, placing the smallest beads at the top of the column and the largest at the bottom. Water was then drained to 1 cm above the adsorbent bed and the bed volume was measured.

The waste stream was pumped through the classified column using a Fluid Metering, Inc. pump and Teflon tubing. Typical flow rates were 1, 2, 3, or 4 gpm/ft^3 (8, 16, 24, or 32 BV/hr). Flows were monitored periodically during the course of each experiment and adjusted as required to maintain a constant flow. Samples for GC analysis were collected periodically in the appropriate vials and analyzed immediately or carefully stored for later analysis (*vide supra*).

When column loading was complete (i.e., at 90 ± 10% breakthrough) the column was drained and regenerant was slowly pumped upflow to about 2 cm above the bed. This displaced air from the bed. Regenerant was then pumped downflow at 1 BV/hr until no pollutant was detected in the effluent. Samples were collected volumetrically in 1/4 BV portions and analyzed by GC. Generally, regeneration was complete in 3 BV or less.

Excellent, illustrated descriptions of laboratory scale column loading and regeneration experiments using synthetic resin adsorbents have been published [2,5].

SECTION 6

RESULTS AND DISCUSSION

ADSORPTION ISOTHERM TESTS

The isotherm test provides a method of predicting an adsorbent's equilibrium capacity for adsorption of specific organics from water over a range of concentrations. This test method was used to generate data for comparison with capacity data obtained using the new batch test method developed during this project.

The adsorption data were plotted according to the log form of the empirical Freundlich equation:

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_f$$

where x = mg compound adsorbed, $[(C_{in}-C_f) \cdot \text{volume}]$
m = g adsorbent
C_f = equilibrium concentration of the solution (mg/L)
C_{in} = initial concentration of the solution (mg/L)
K,n = constants

The data were fitted by least squares linear regression analysis of the log form of the Freundlich equation to locate the isotherm line. The fit of the data to this line is indicated by the correlation coefficient R. When R=1 there is a perfect fit. When R=0 there is no correlation between the data and the line. The constant K represents the capacity (mg compound adsorbed per g adsorbent) at an equilibrium concentration of 1 ppm. These K values are usually an extrapolation of the data by at least a factor of 10. 1/n, the slope of the line, is an indicator of adsorption intensity. A low slope indicates low sensitivity to concentration changes. Generally, the polymeric absorbents are much more sensitive to concentration changes than the carbonaceous adsorbents (i.e. the slopes of their isotherms are much greater).

Filtrasorb 300 carbon adsorption isotherms for a large number of toxic organics have been reported [9]. The work was done under very different experimental conditions than the isotherm tests reported here: the carbon was pulverized, screened to 200-400 mesh, and slurried before use; equilibration time was 2 to 3 hours; initial solution concentration was less than 10 ppm; and carbon dosage was low (0.001 to 0.5 g/L). Since isotherms are not strictly linear over large concentration ranges (i.e. 10^2-10^3), it is not realistic to expect linearity over the large concentration range represented by these three studies (i.e. .001 to 2000 ppm). Thus, carbon adsorption isotherms for the pollutants reported in this study cannot be compared to previously reported data.

2-Nitrophenol

Adsorption isotherms for 2-nitrophenol (NPL) in water buffered at pH 5 and pH 8 are shown in Figures 1 and 2, respectively for the Amberlite adsorbents. At pH 5, NPL ($Ka=6.8 \times 10^{-8}$) is almost entirely in its neutral form while at pH 8 the ratio of weak acid to conjugate base (anion) is 1:7. In addition to the non-functionalized, high surface area adsorbents tested, two very low surface area, weak base ion exchange resins were also tested (i.e. Amberlites IRA-45 and IRA-93). The Freundlich parameters obtained from linear regression analyses of the isotherm data are recorded in Table 2. Assuming isotherm linearity, adsorption capacities at selected concentrations of NPL from 10 to 1000 ppm were calculated from the Freundlich parameters and are recorded in Table 3.

The effect of pH on adsorption capacity is marked. All the resins have higher capacities at the lower pH where NPL is in its neutral form. In this NPL concentration range, XAD-4 is the best Amberlite adsorbent tested. These results indicate that surface area effects (adsorption via Van der Waals forces) predominate over the ionic interaction occurring in the adsorption of polarized weak acid NPL by the amine-containing weak base resins (adsorption via hydrogen bonding) [6,10,11].

Diaion adsorbents were not available for testing at the time these experiments were performed. Difficulties in pH control and dosage levels gave rise to very erratic data during testing with carbonaceous adsorbents. Thus, no isotherm data are reported for those adsorbents.

Tetrachloroethylene

Due to problems with the electron capture detector of the GC, the tetrachloroethylene isotherm data are highly unreliable and are not reported here. However, batch/rate data are acceptable and are reported in a later section.

Nitrobenzene

Adsorption isotherms for nitrobenzene (NB) in water are shown in Figures 3, 4, and 5 for the Amberlite, Diaion, and carbonaceous adsorbents respectively. Freundlich parameters are recorded in Table 4 and calculated equilibrium adsorption capacities at selected NB concentrations are recorded in Table 5. Since the plotted data are not linear (see Figures), extrapolation of the linear isotherm data below 10 ppm and above 1000 ppm leads to inaccurate capacity data. For Diaion HP-20 at 1900 ppm NB (influent concentration), the calculated capacity is 670 mg/g but the capacity obtained graphically from a "best fit" curve is 910 mg/g. Similarly for Amberlite XAD-4, at 1900 ppm NB, the calculated capacity is 859 mg/g but the capacity obtained graphically is 1050 mg/g.

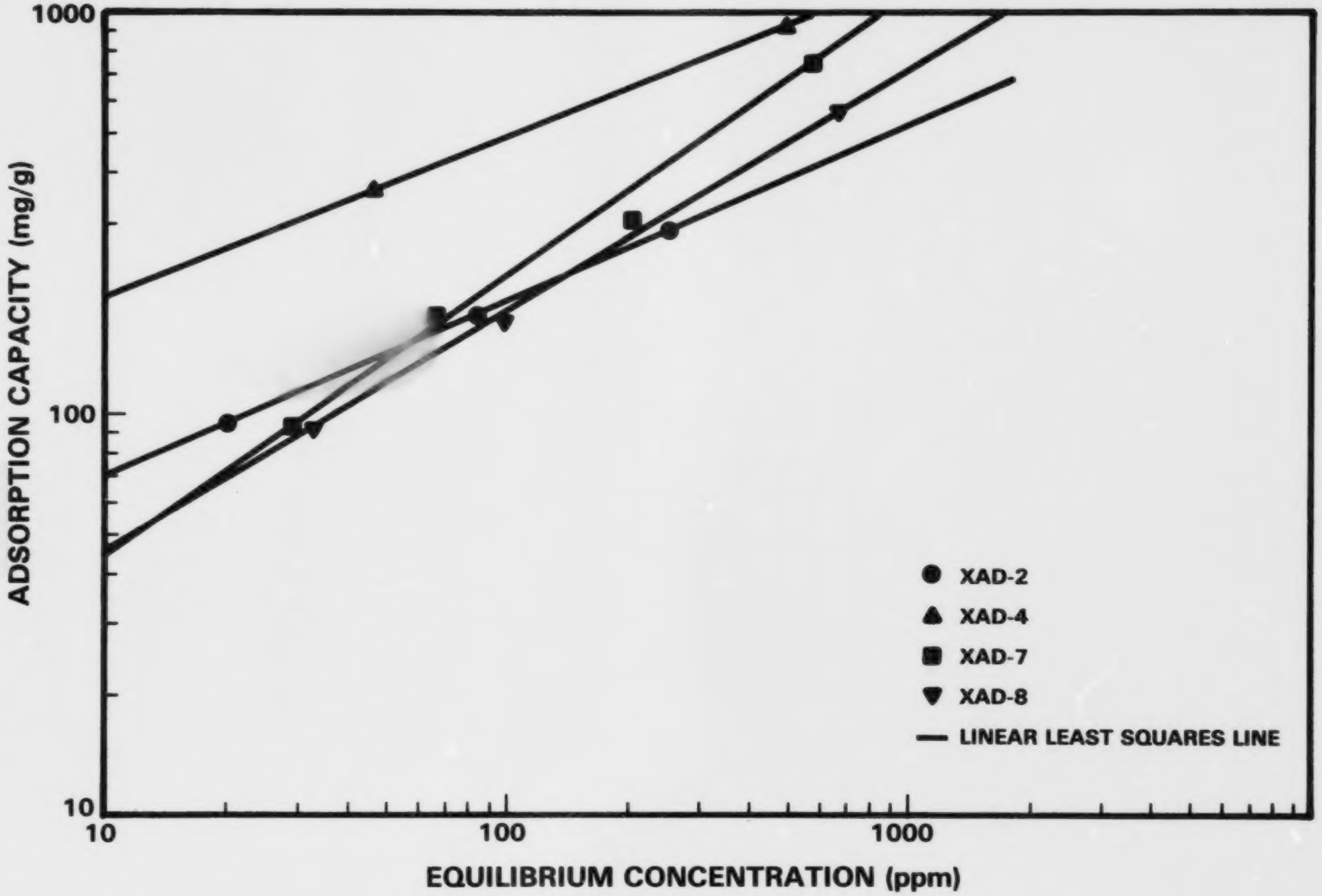


FIGURE 1. ADSORPTION ISOTHERMS FOR 2-NITROPHENOL (pH 5) ON AMBERLITE ADSORBENTS

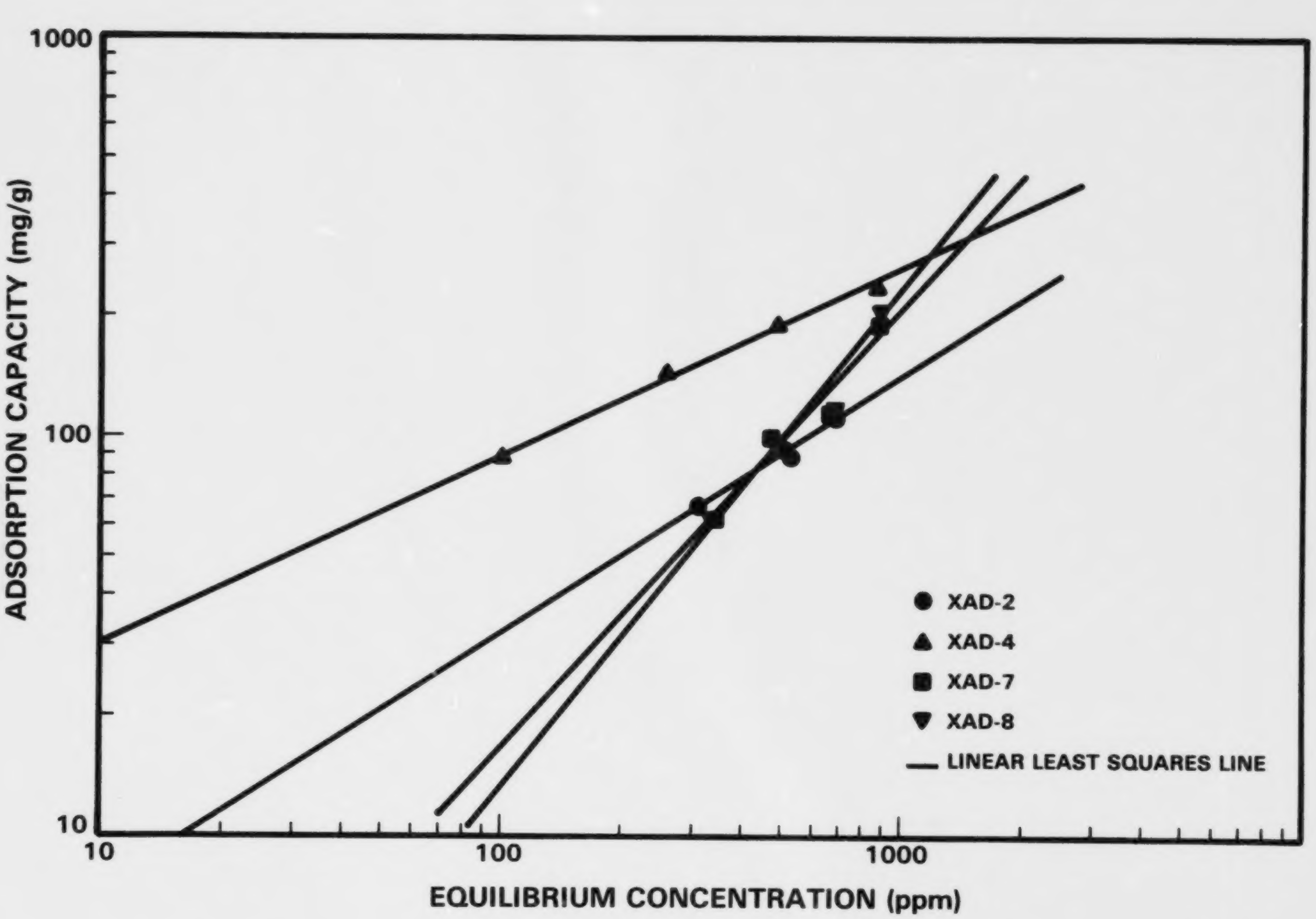


FIGURE 2. ADSORPTION ISOTHERMS FOR 2-NITROPHENOL (pH 8) ON AMBERLITE ADSORBENTS

TABLE 2

ADSORPTION ISOTHERM TESTING WITH 2-NITROPHENOL

		Freundlich Parameters		
Adsorbent	pH	Corr. Coef.(R)	1/n	K[a]
XAD-2	5	1.000	0.440	25.1
XAD-2	8	0.989	0.639	1.7
XAD-4	5	1.000	0.410	74.3
XAD-4	8	0.997	0.470	10.2
XAD-7	5	0.993	0.679	9.5
XAD-7	8	0.962	1.079	0.1
XAD-8	5	0.998	0.605	10.8
XAD-8	8	0.954	1.234	0.0
IRA-45	5	0.960	0.566	12.7
IRA-45	8	0.969	0.563	9.4
IRA-93	5	0.995	0.569	9.8
IRA-93	8	0.980	1.057	0.3

[a] K is equal to the equilibrium adsorption capacity at a residual concentration of 1 ppm.

TABLE 3

ADSORPTION CAPACITIES FOR 2-NITROPHENOL MEASURED BY ISOTHERM TESTS[a]

		Equilibrium Adsorption Capacity (mg/g)[b]			
Adsorbent	pH	at 10 ppm	at 100 ppm	at 750 ppm	at 1000 ppm
XAD-2	5	69	190	462	524
XAD-2	8	7	32	116	139
XAD-4	5	191	491	1120	1260
XAD-4	8	30	89	228	261
XAD-7	5	45	217	852	1040
XAD-7	8	1	17	148	202
XAD-8	5	43	175	592	704
XAD-8	8	1	13	159	227
IRA-45	5	47	172	538	633
IRA-45	8	34	126	390	459
IRA-93	5	36	140	421	496
IRA-93	8	4	43	365	495

[a] The initial concentration of aqueous 2-nitrophenol solution was 975 ± 25 ppm and equilibrium concentrations were in the range of 20 to 900 ppm.

[b] The capacities are calculated from the Freundlich parameters obtained from a linear regression analysis of the isotherm data.

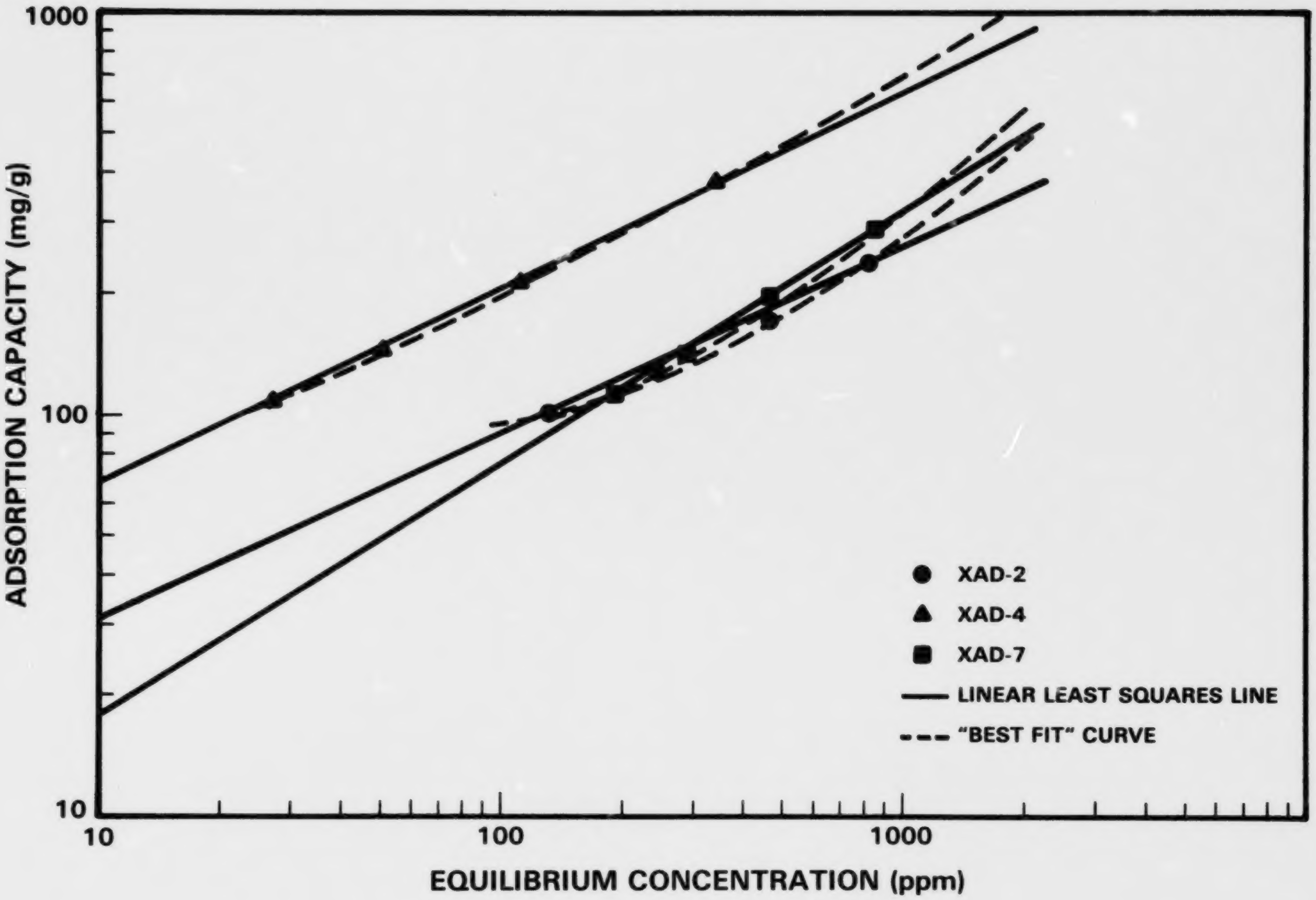


FIGURE 3. ADSORPTION ISOTHERMS FOR NITROBENZENE ON AMBERLITE ADSORBENTS

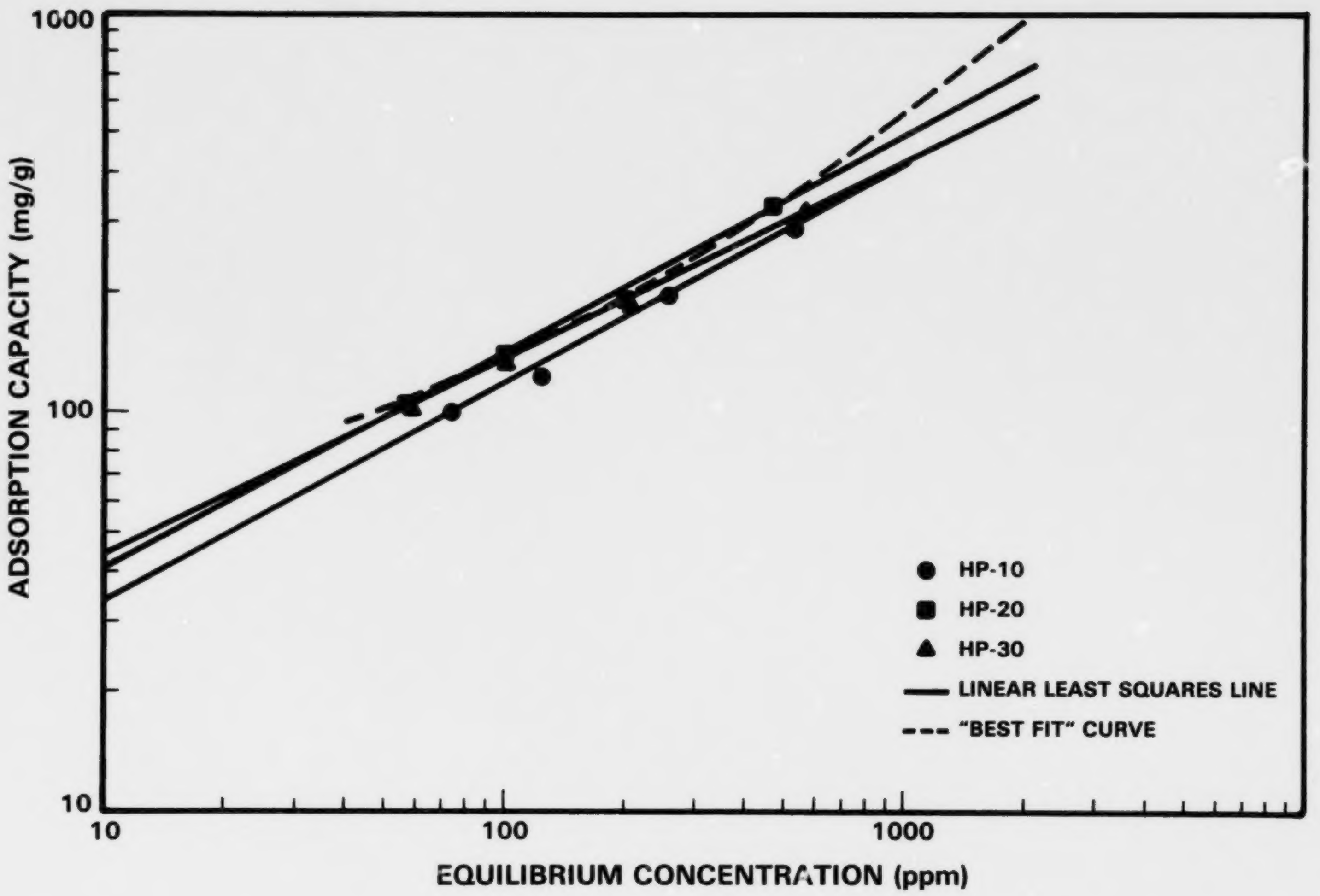


FIGURE 4. ADSORPTION ISOTHERMS FOR NITROBENZENE ON DIAION ADSORBENTS

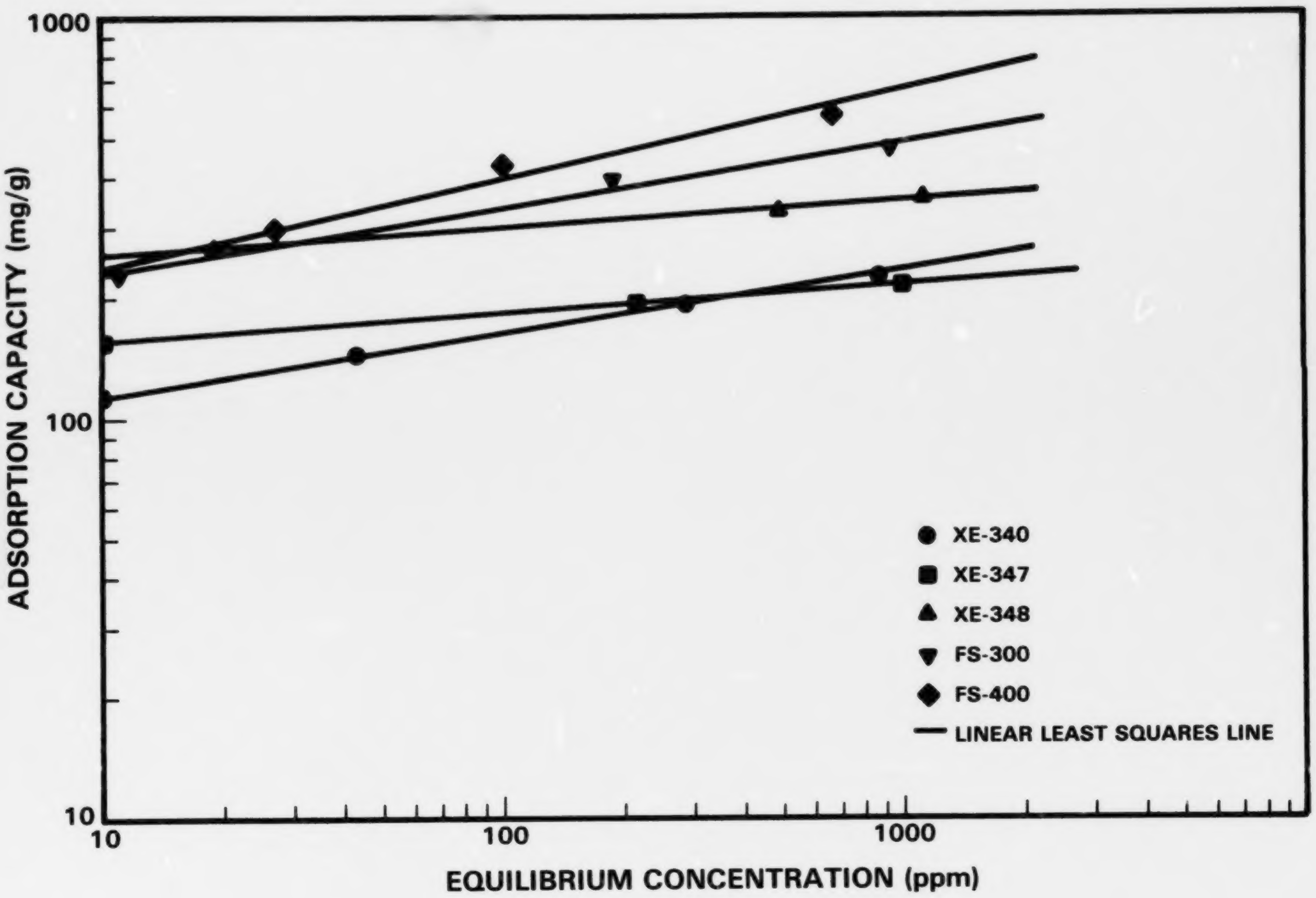


FIGURE 5. ADSORPTION ISOTHERMS FOR NITROBENZENE ON CARBONACEOUS ADSORBENTS

TABLE 4

ADSORPTION ISOTHERM TESTING WITH NITROBENZENE

Adsorbent	Freundlich Parameters		
	Corr. Coef.(R)	1/n	K[a]
HP-10	1.000	0.539	9.90
HP-20	0.997	0.533	11.9
HP-30	0.999	0.491	14.1
XAD-2	0.995	0.469	10.0
XAD-4	0.999	0.487	21.8
XAD-7	1.000	0.623	4.22
XAD-8	0.998	0.630	3.91
XE-340	0.999	0.163	76.9
XE-347	0.998	0.0665	135
XE-348	0.994	0.0688	217
FS-300	0.990	0.168	155
FS-400	0.988	0.223	142

[a] K is equal to the equilibrium adsorption capacity at a residual concentration of 1 ppm.

TABLE 5

ADSORPTION CAPACITIES FOR NITROBENZENE MEASURED BY ISOTHERM TESTS[a]

Adsorbent	Equilibrium Adsorption Capacity (mg/g)[b] at 10 ppm	at 100 ppm	at 1000 ppm	at 1900 ppm
HP-10	34	118	409	578
HP-20	41	139	475	670
HP-30	44	135	417	571
XAD-2	29	90	255	345
XAD-4	70	205	628	859
XAD-7	18	74	312	467
XAD-8	17	71	304	456
XE-340	119	163	236	262
XE-347	158	183	214	222
XE-348	255	298	350	365
FS-300	228	336	494	551
FS-400	236	394	659	760

[a] The initial concentration of the aqueous nitrobenzene solution was 1900 ppm and equilibrium concentrations were in the range of 10-1000 ppm.

[b] The capacities are calculated from the Freundlich parameters obtained from a linear regression analysis of the isotherm data.

The results of this isotherm testing indicate that at high NB concentrations (e.g. >1000 ppm), Amberlite XAD-4 is the best adsorbent. At low concentrations (e.g. <100 ppm) the activated carbon Filtrasorb-400 is the best adsorbent.

Based on the results of the NPL and NB isotherm studies, only a representative group of the 12 available adsorbents were selected for further testing. The 6 adsorbents chosen include Diaion HP-20, Amberlites XAD-4 and XAD-7, Ambersorbs XE-340 and XE-348, and Filtrasorb 400. These were considered to be the best representatives of their particular class (see Table 1).

1,2-Dichloropropane

Adsorption isotherms for 1,2-dichloropropane (PDC) in water appear in Figures 6 and 7 for the polymeric and carbonaceous adsorbents respectively. Freundlich parameters, obtained from linear regression analyses of the data, are recorded in Table 6. Assuming isotherm linearity, adsorption capacities at selected equilibrium concentrations of PDC were calculated from these Freundlich parameters and are recorded in Table 7. Again the plotted data show nonlinearity so both the linear least squares lines and the "best fit" curves are displayed. Extrapolation of least squares data to predict adsorption capacity at initial waste stream concentration (2500 ppm) produces inaccurate capacity data. For example, for XAD-4 at 2500 ppm PDC, linear extrapolation predicts a capacity of 747 mg/g while curved extrapolation predicts a capacity of 1000 mg/g.

At very high PDC concentrations (e.g. >1500 ppm) the polymeric adsorbents Diaion HP-20 and Amberlite XAD-4 have the highest capacities. At intermediate PDC concentrations (e.g. 100-1000 ppm), the activated carbon Filtrasorb 400 is the best adsorbent.

2,4-Dinitrotoluene

Adsorption isotherms for 2,4-dinitrotoluene (DNT) in water are shown in Figures 8 and 9 for the polymeric and carbonaceous adsorbents respectively. Freundlich parameters are listed in Table 8 and the calculated adsorption capacities at selected DNT concentrations are listed in Table 9. The correlation coefficients are excellent and the data appear to be more linear than in the previous studies. However, the concentration range in the DNT study is about a factor of 10 less (i.e., 150 ppm versus 1500 ppm).

Filtrasorb 400 is the best adsorbent over the entire concentration range. At high DNT concentrations, the polymeric adsorbents Diaion HP-20 and Amberlite XAD-4 also have good capacities.

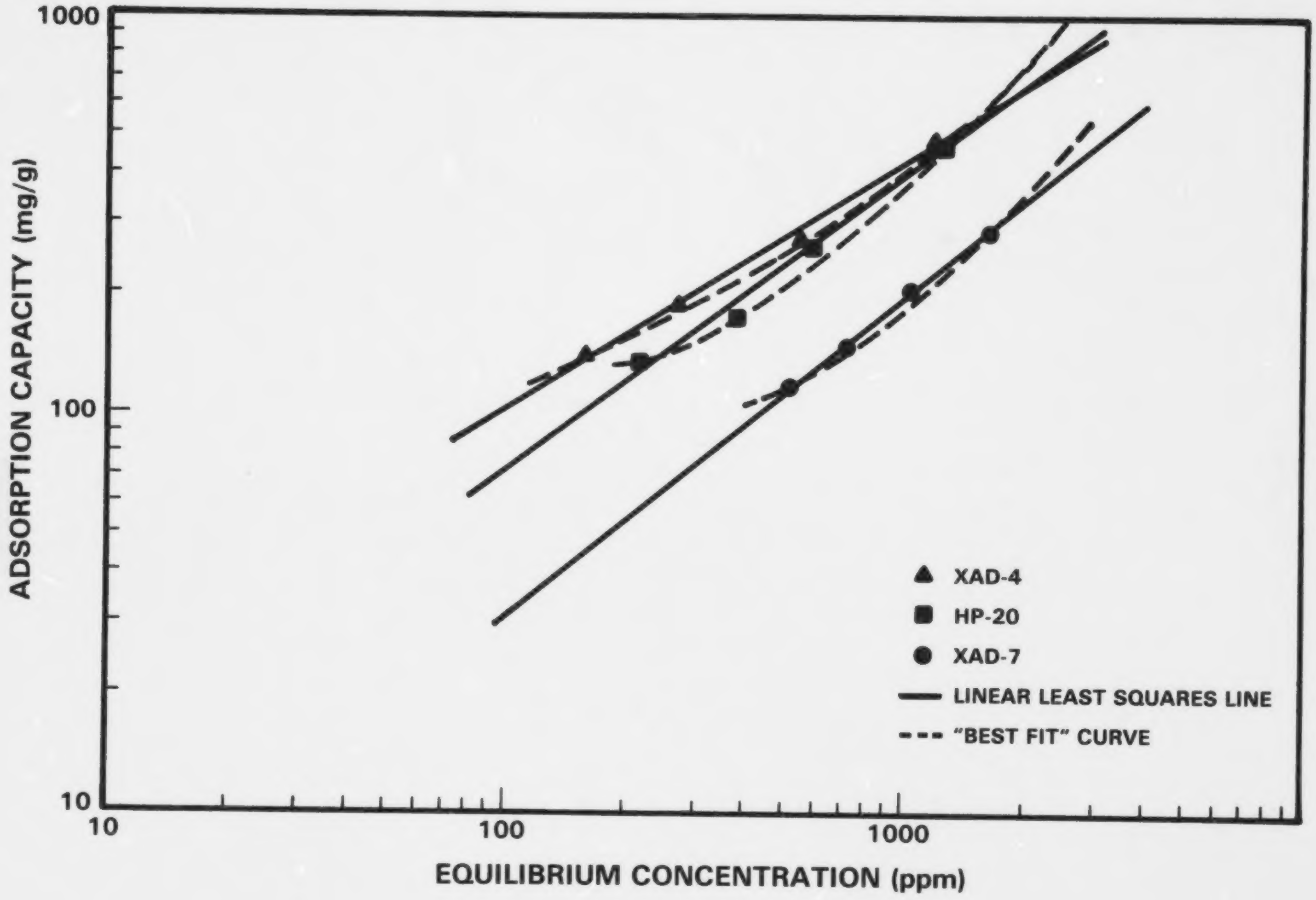


FIGURE 6. ADSORPTION ISOTHERMS FOR 1,2-DICHLOROPROPANE ON POLYMERIC ADSORBENTS

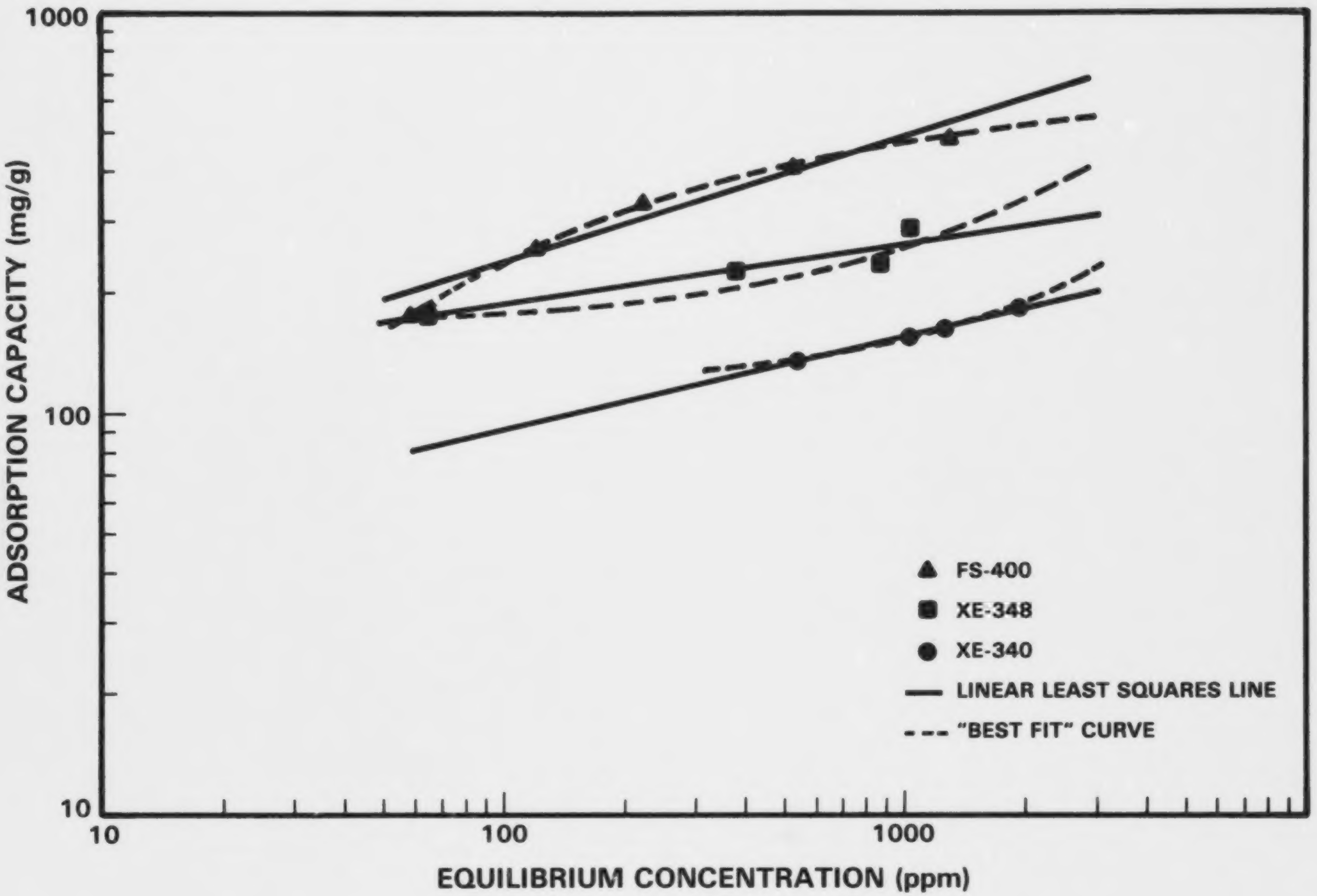


FIGURE 7. ADSORPTION ISOTHERMS FOR 1,2-DICHLOROPROPANE ON CARBONACEOUS ADSORBENTS

TABLE 6

ADSORPTION ISOTHERM TESTING WITH 1,2-DICHLOROPROPANE

	Freundlich Parameters		
Adsorbent	Corr. Coef.(R)	1/n	K[a]
HP-20	0.991	0.743	2.3
XAD-4	0.995	0.619	5.9
XAD-7	0.999	0.801	0.8
XE-340	0.990	0.230	31.5
XE-348	0.912	0.142	97.8
FS-400	0.975	0.315	54.6

[a] K is equal to the equilibrium adsorption capacity at a residual concentration of 1 ppm.

TABLE 7

ADSORPTION CAPACITIES FOR 1,2-DICHLOROPROPANE MEASURED BY ISOTHERM TESTS[a]

	Equilibrium Adsorption Capacity (mg/g)[b]		
Adsorbent	at 100 ppm	at 1000 ppm	at 2500 ppm
HP-20	71	394	778
XAD-4	102	424	747
XAD-7	31	196	409
XE-340	91	154	190
XE-348	188	262	298
FS-400	233	482	644

[a] The initial concentration of aqueous 1,2-dichloropropane solution was 2330 ppm and equilibrium concentrations were in the range of 50-2000 ppm.

[b] The capacities are calculated from the Freundlich parameters obtained from a linear regression analysis of the isotherm data.

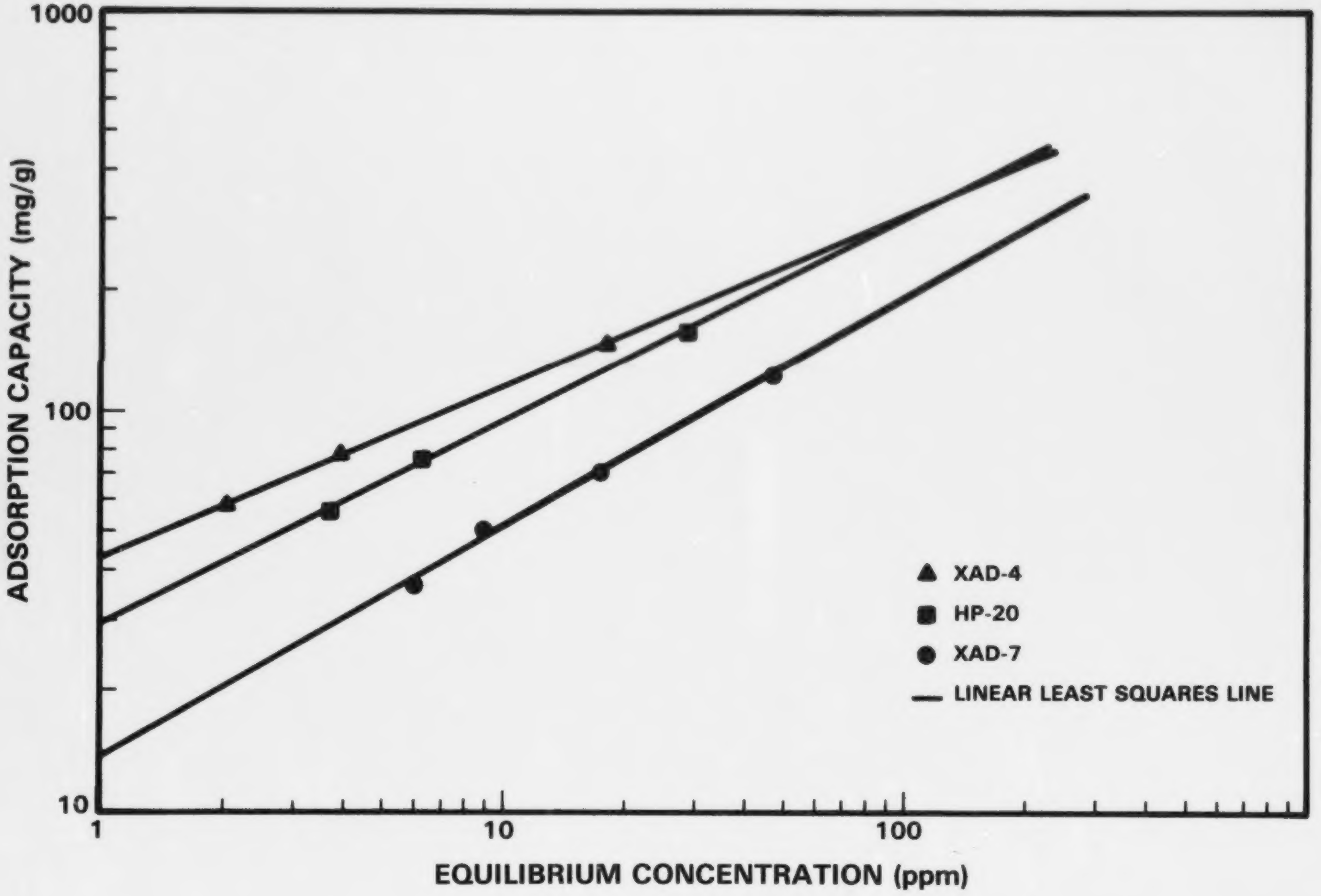


FIGURE 8. ADSORPTION ISOTHERMS FOR 2,4-DINITROTOLUENE ON POLYMERIC ADSORBENTS

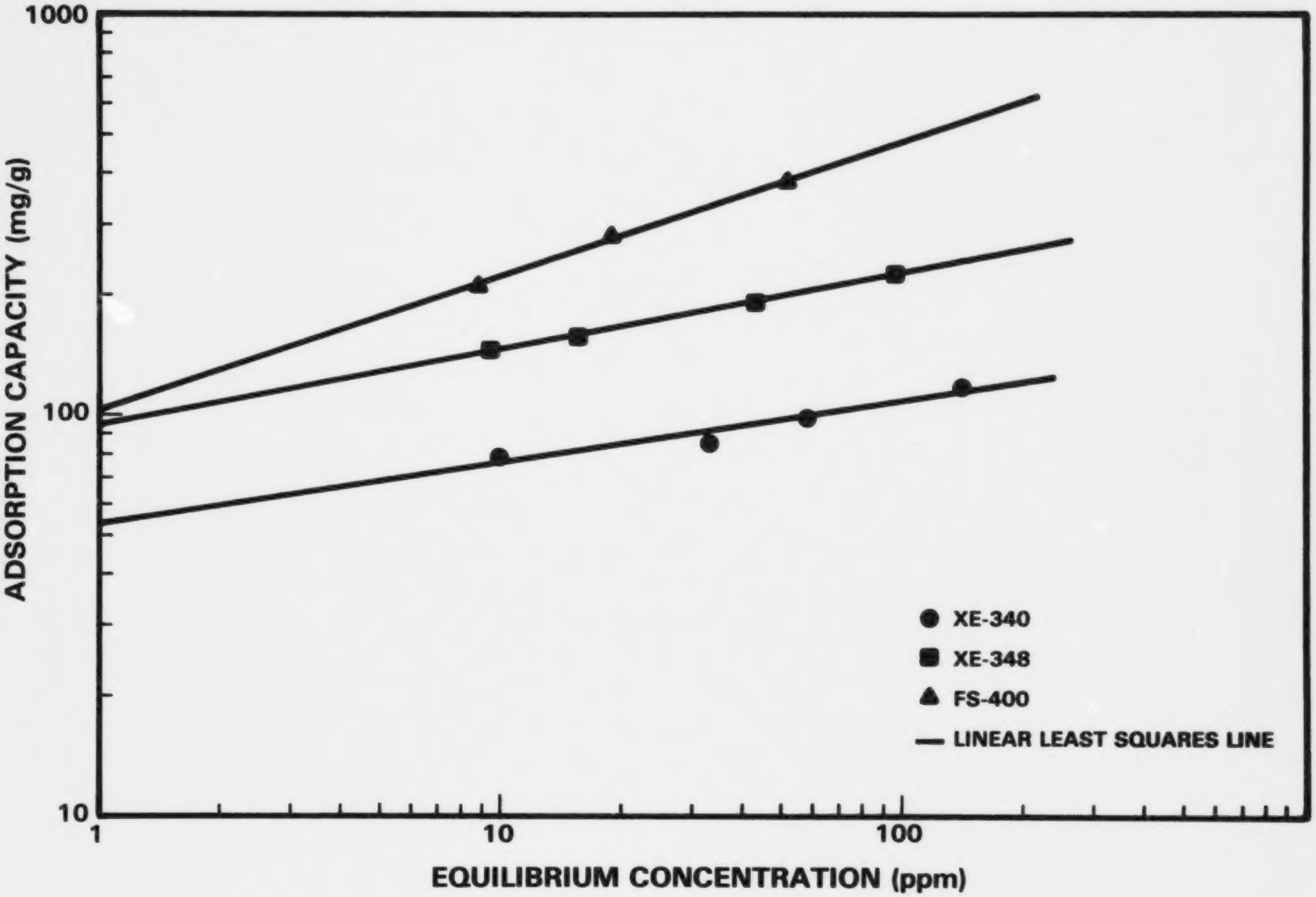


FIGURE 9. ADSORPTION ISOTHERMS FOR 2,4-DINITROTOLUENE ON CARBONACEOUS ADSORBENTS

TABLE 8

ADSORPTION ISOTHERM TESTING WITH 2,4-DINITROTOLUENE

	Freundlich Parameters		
Adsorbent	Corr. Coef.(R)	1/n	K[a]
HP-20	0.998	0.504	29.5
XAD-4	1.000	0.431	42.2
XAD-7	0.998	0.569	13.8
XE-340	0.959	0.154	53.2
XE-348	1.000	0.187	95.5
FS-400	0.997	0.333	104

[a] K is equal to the equilibrium adsorption capacity at a residual concentration of 1 ppm.

TABLE 9

ADSORPTION CAPACITIES FOR 2,4-DINITROTOLUENE MEASURED BY ISOTHERM TESTS[a]

	Equilibrium Adsorption Capacity (mg/g)[b]			
Adsorbent	at 1 ppm	at 10 ppm	at 100 ppm	at 180 ppm
HP-20	29.5	94.1	300	403
XAD-4	42.2	114	308	397
XAD-7	13.8	51.2	190	265
XE-340	53.2	75.9	108	118
XE-348	95.5	147	226	252
FS-400	104	224	483	587

[a] The initial concentration of aqueous 2,4-dinitrotoluene solution was 180 ± 10 ppm and equilibrium concentrations were in the range of 1–140 ppm.

[b] The capacities are calculated from the Freundlich parameters obtained from a linear regression analysis of the isotherm data.

BATCH/RATE TESTS

The batch/rate test consists of exposing bags of various adsorbents to a waste stream for a selected period of time. The exposed adsorbents are then regenerated, typically using organic solvents, steam, or caustic, and the regenerated adsorption capacities are obtained. In the batch portion of the test, the adsorbents are exposed to the waste stream sufficiently long enough to saturate each adsorbent with pollutants. The regenerated adsorption capacity at saturation, as obtained from the batch test, is a measure of maximum column capacity. The batch capacity data are compared and used as guide for selecting the optimum adsorbent(s) for additional testing in the waste stream. In the rate portion of the test, bags of the optimum adsorbent(s) are exposed to the waste stream and removed as time passes, prior to adsorbent saturation. From the amount adsorbed (i.e. regenerated) as a function of time, the mass transfer coefficient is calculated. Using data provided by batch/rate studies (i.e. saturation capacity and mass transfer coefficient) column performance can be predicted under a variety of column operating conditions.

During the course of this study, the batch/rate test procedures were refined. Thus, data obtained during the NPL study (the first study) are not as reliable as those obtained in the PDC study (the fourth study). When testing is done in a limited volume waste stream (such as the 5L reservoir of the synthetic waste stream system), only 2 to 5 bags of adsorbent should be tested simultaneously. Too much adsorbent can significantly depress the reservoir concentration which ideally should remain nearly constant. This should not be a problem in testing real waste streams if bags of adsorbent can be placed into a constantly flowing stream. When the bags are removed from the waste stream, the adsorbent should be drained and either regenerated immediately or stored in small, tightly sealed bottles with a minimum of air space until regeneration is performed. This minimizes loss of compound due to volatility.

The polymeric adsorbents usually regenerate well with organic solvents (e.g. methanol, acetone, toluene). Their regenerated saturation capacities are often higher than predicted by extrapolation of linear isotherm lines to influent concentrations. As previously discussed, isotherm data cannot be accurately extrapolated due to isotherm nonlinearity over large concentration ranges. The carbonaceous adsorbents usually have lower regenerated saturation capacities than predicted by isotherm tests due to incomplete regeneration by organic solvents under the chosen regeneration conditons.

During the rate test the adsorbent must be well agitated. By using a fast stirring rate ($\geq$400 rpm) and spacious "tea bags" the influences of diffusion through bulk solution and adsorbent packing on the rate of adsorption (mass transfer coefficient) are minimized. Due to experimental design, very short adsorption times (less than 10 minutes) can result in highly scattered data. Good kinetic data should be fairly linear or follow a smooth curve during the first 10 to 90 minutes of adsorption.

2-Nitrophenol

The results of the batch test adsorption of NPL from water buffered at pH 5 and pH 8 are reported in Table 10. Samples of each adsorbent were regenerated with methanol and with acetone. The capacities obtained by regeneration with these two solvents generally agree except for studies with the weak base resins, IRA-45 and IRA-93. The data are somewhat scattered, but methanol appears to be a more effective regenerant than acetone for the weak base resins. As was noted in the isotherm results section, the polymeric adsorbents have significantly higher NPL capacity at lower pH. However, for the activated carbon FS-400, pH has much less effect on capacity, concurring with previous findings for adsorption of NPL by carbon [9]. Amberlite XAD-4 and Filtrasorb 400 have the highest regenerated saturation capacities.

During the NPL adsorption study, the first application of the new batch/rate test method, a number of experimental difficulties were encountered. The test method was refined and resulting procedural changes were incorporated in later studies with other compounds. The lack of precision in the NPL data is primarily due to very small sample size (i.e. 10 to 30 mg adsorbent and 1 to 2 mL regenerant).

Comparison of NPL adsorption data for the XAD resins obtained by batch testing (Table 10) and isotherm testing (Table 3, at 750 ppm) reveals some discrepancy. The results obtained at pH 8 agree satisfactorily, allowing for experimental problems encountered in batch testing (vide supra). However, at pH 5, batch results (saturation capacities measured by regenerating the adsorbents) are a factor of 2 or 3 lower than isotherm results (saturation capacities measured by concentration changes of the waste stream). This indicates that the adsorbents were not regenerated completely. Since both isotherm and batch results indicate that the conjugate base of NPL is less well adsorbed than the neutral molecule, caustic would be good regenerant to study. Related studies of p-nitrophenol adsorption on synthetic resins confirm this [6,10]. Regeneration of adsorbents plays a critical role in the economics of waste water treatment by adsorbents. The batch/rate test method provides a relatively simple means of assessing both adsorbent capacity and regeneration ease, whereas the isotherm test method measures capacity only.

Rate test results for adsorption of 2-nitrophenol by XAD-4 at pH 5 and pH 8 are recorded in Table 11 and plotted in Figure 10. The rate of uptake of NPL is initially much faster at pH 5 than at pH 8. The tests were performed under conditions of decreasing NPL concentration with increasing time, and the data do not extrapolate well to equilibrium (batch) capacities. This portion of the batch/rate test was also revised for later studies with other compounds.

Tetrachloroethylene

Batch test results for adsorption of tetrachloroethylene (TETRA) from water are listed in Table 12. XAD-4 has the highest methanol regenerated capacity of any of the adsorbents tested (1170 mg/g).

TABLE 10

ADSORPTION CAPACITIES FOR 2-NITROPHENOL MEASURED BY BATCH TESTS[a]

Adsorbent	pH	Methanol Regenerated Adsorption Capacity (mg/g)	Acetone Regenerated Adsorption Capacity (mg/g)
XAD-2	5	199	207
XAD-2	8	149	139
XAD-4	5	518	519
XAD-4	8	311	386
XAD-7	5	204	270
XAD-7	8	157	148
XAD-8	5	242	247
XAD-8	8	153	136
IRA-45	5	75	109
IRA-45	8	134	35
IRA-93	5	123	63
IRA-93	8	261	119
XE-340	5	189	189
XE-340	8	150	175
XE-348	5	164	242
XE-348	8	68	139
FS-400	5	485	402
FS-400	8	477	498

[a] Final 2-nitrophenol concentration was 750 ppm at pH 5 and 820 ppm at pH 8.

TABLE 11

RATE TEST RESULTS FOR ADSORPTION OF 2-NITROPHENOL BY XAD-4[a]

Time (min.)	pH	Methanol Regenerated Adsorption Capacity (mg/g)
5	5	124
20	5	354
60	5	395
5	8	51
20	8	89
75	8	183

[a] Final 2-nitrophenol concentration was 770 ppm at pH 5 and 950 ppm at pH 8.

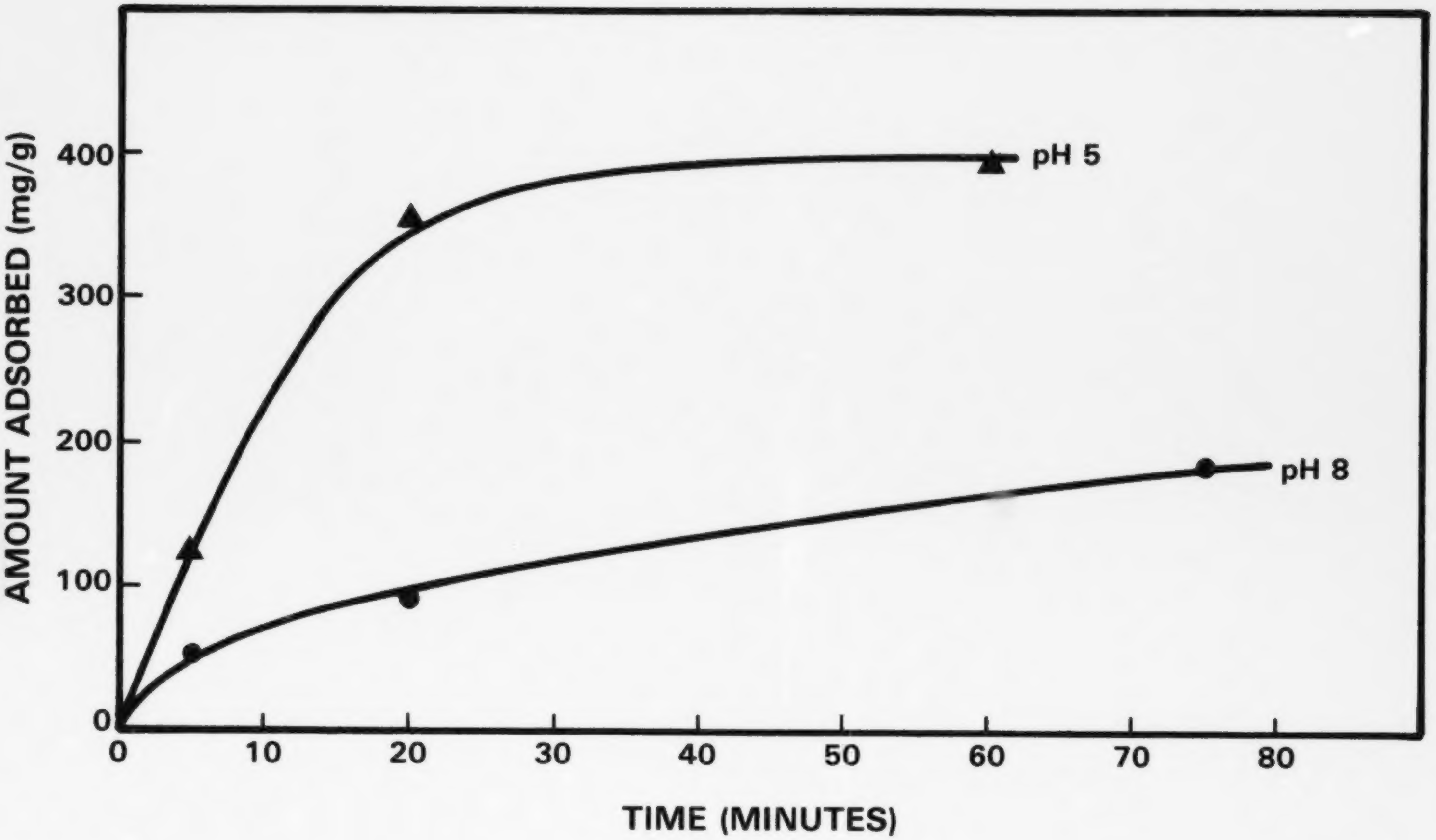


FIGURE 10. RATE OF ADSORPTION OF 2-NITROPHENOL BY AMBERLITE XAD-4

Results of rate testing for adsorption of TETRA by XAD-4 are reported in Table 13 and plotted in Figure 11. The rate of adsorption increases linearly with time over the first 60 minutes. Regression analysis yields an adsorption rate of 0.8 mg/g-min. This corresponds to a mass transfer coefficient of 0.0053 L/g-min assuming an influent concentration of 150 mg/L.

Nitrobenzene

The results of batch test adsorption of nitrobenzene (NB) from water are reported in Table 14. Twelve adsorbents were tested and methanol was selected as the regenerant. Although methanol proved to be a very good regenerant, methanol may not be the optimum regenerant. Other solvents which might be tested include acetone and toluene. The polymeric adsorbents regenerated better with methanol than either the carbonaceous adsorbents or activated carbons. XAD-4 has the highest methanol regenerated capacity (1310 mg/g), but both HP-10 (1140 mg/g) and HP-20 (1160 mg/g) also perform well.

Comparison of the NB capacity data obtained from isotherm testing (Table 5, at 1900 ppm) and batch testing (Table 14) reveals that the batch tests predict much higher adsorption capacities for polymeric adsorbents than isotherm tests do. This discrepancy is due to the extrapolation of isotherm data from the equilibrium concentration range of 10 to 1000 ppm to the influent concentration of 1900 ppm. The inaccuracy of such extrapolation was discussed previously.

Rate test results for adsorption of nitrobenzene by XAD-4 are listed in Table 15 and plotted in Figure 12. The rate test was repeated. Due to improper storage of the samples, data from the first kinetic study did not extrapolate well to the equilibrium adsorption capacity of 1310 mg/g. Data measured at very short contact times (<10 minutes) were omitted from linear regression analysis due to their non-reproducibility. For 6 points obtained during the first hour, regression analysis yields a rate of adsorption of 3.19 mg/g-min with a correlation coefficient of 0.98. Using this rate of adsorption, a mass transfer coefficient of 0.00168 L/g-min is calculated assuming an influent concentration of 1900 mg/L. Within the first hour of exposure to the 1900 ppm NB stream, XAD-4 has attained 50% of its saturation capacity.

1,2-Dichloropropane

The results of batch test adsorption of 1,2-dichloropropane (PDC) are reported in Table 16. Samples of each saturated adsorbent were regenerated with methanol and acetone. The capacities obtained by regeneration with these solvents are identical within experimental error (i.e., ±5% of the average). Batch results again do not correlate well with capacities calculated from Freundlich parameters (Table 7, at 2500 ppm). However, batch capacities for the polymeric adsorbents do agree fairly well with capacities predicted by curve fitting of the isotherm data (see Figure 6). The best adsorbents are Diaion HP-20 and Amberlite XAD-4 with regenerated saturation capacities of 1075 ± 15 mg/g and 1055 ± 25 mg/g respectively.

TABLE 12

ADSORPTION CAPACITIES FOR TETRACHLOROETHYLENE MEASURED BY BATCH TESTS[a]

Adsorbent	Methanol Regenerated Adsorption Capacity (mg/g)
XAD-2	966
XAD-4	1170
XAD-7	438
XAD-8	360
XE-340	330
XE-347	466
XE-348	676

[a] Initial tetrachloroethylene concentration was 150 ppm.

TABLE 13

RATE TEST RESULTS FOR ADSORPTION OF TETRACHLOROETHYLENE BY XAD-4[a]

Time (min.)	Methanol Regenerated Adsorption Capacity (mg/g)
3	3.0
5	5.3
7	6.2
10	8.0
15	10.8
23	23.1
40	30.5

[a] Initial tetrachloroethylene concentration was 150 ppm.

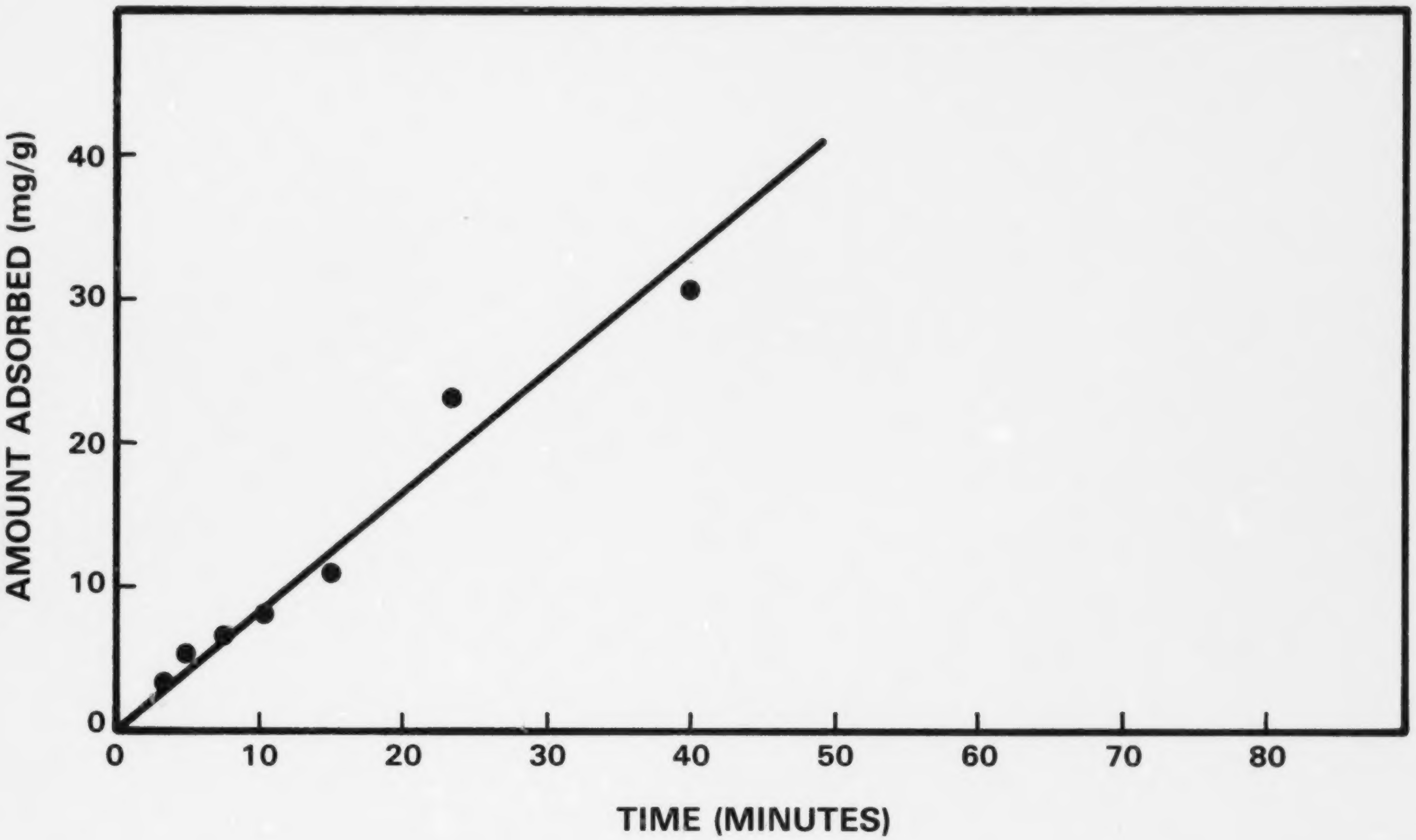


FIGURE 11. RATE OF ADSORPTION OF TETRACHLOROETHYLENE BY AMBERLITE XAD-4

TABLE 14

ADSORPTION CAPACITIES FOR NITROBENZENE MEASURED BY BATCH TESTS[a]

Adsorbent	Methanol Regenerated Adsorption Capacity (mg/g)
HP-10	1140
HP-20	1160
HP-30	706
XAD-2	699
XAD-4	1310
XAD-7	881
XAD-8	580
XE-340	283
XE-347	179
XE-348	241
FS-300	406
FS-400	537

[a] Nitrobenzene concentration was maintained at 1890 ± 30 ppm.

TABLE 15

RATE TEST RESULTS FOR ADSORPTION OF NITROBENZENE BY XAD-4[a]

Time (min.)	Methanol Regenerated Adsorption Capacity (mg/g)
1st Kinetic Run	
5	496
15	546
30	593
45	653
97	747
247	917
420	937
1440	1020
2nd Kinetic Run	
6	186
18	567
35	634
55	673
196	1083

[a] Nitrobenzene concentration was maintained at 1890 ± 30 ppm.

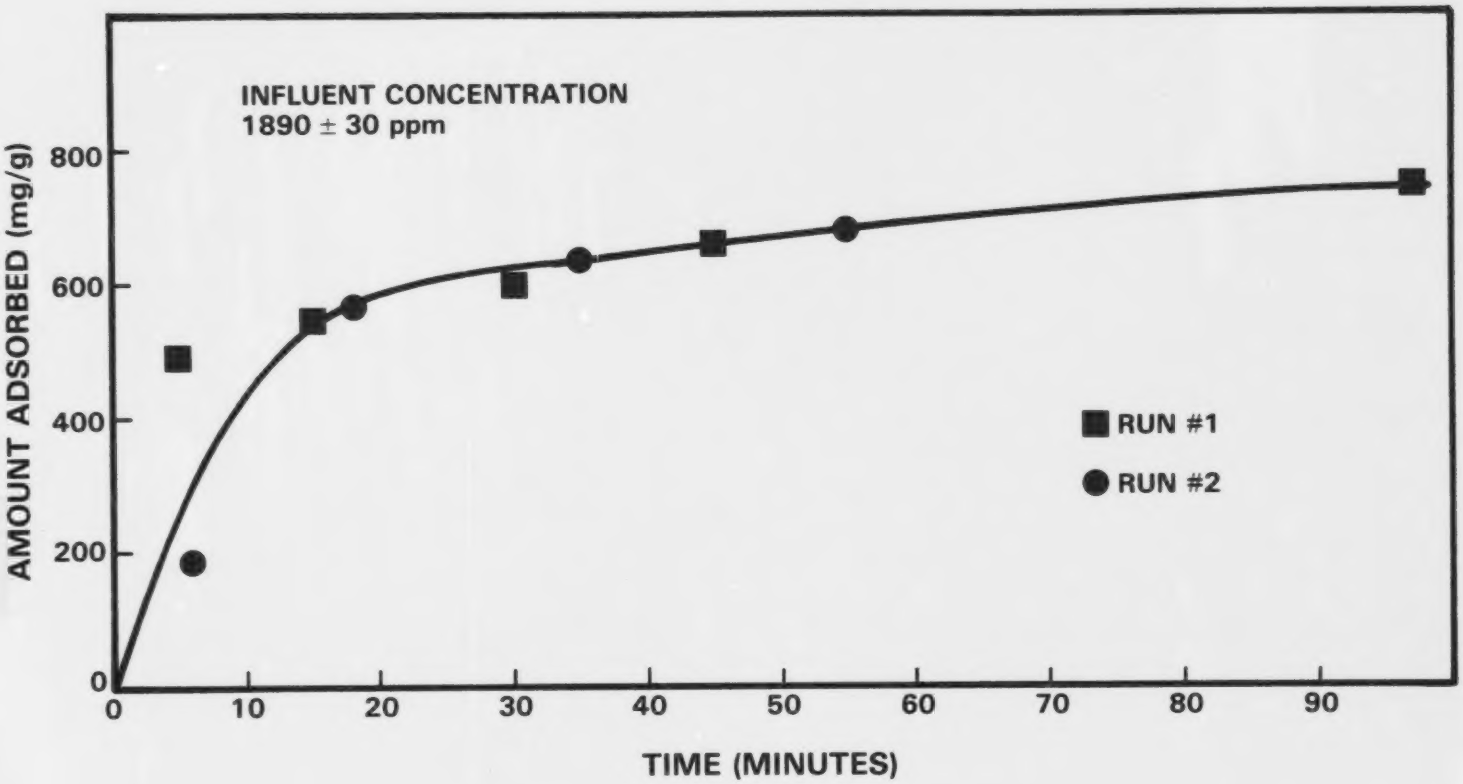


FIGURE 12. RATE OF ADSORPTION OF NITROBENZENE BY AMBERLITE XAD-4

Although isotherm results predict that Ambersorb XE-348 has a saturation capacity significantly greater than Ambersorb XE-340, the regenerated capacities of these adsorbents are essentially identical. This is true for nitrobenzene adsorption as well as 1,2-dichloropropane adsorption. The discrepancy is believed to be due to the different chemical and physical properties of these two carbonaceous adsorbents. XE-340 is less polar and has a higher percentage of larger pores than XE-348[4]. After exposure to the particular organics investigated in this study, XE-340 is completely regenerated by organic solvent but XE-348 is not. Solvent also efficiently regenerates the polymeric adsorbents.

XAD-4 was chosen as the adsorbent for use in the rate test. Results of this study are recorded in Table 17 and plotted in Figure 13. A linear regression analysis of the data from 27 to 99 minutes yields an adsorption rate of 1.90 mg/g-min. This corresponds to a mass transfer coefficient of .00076 L/g-min in the 2500 ppm PDC stream. The rate of approach to equilibrium is rapid. After one hour of exposure to the 2500 ppm PDC stream, XAD-4 has attained about 70% of its saturation capacity.

2,4-Dinitrotoluene

The results of the batch test adsorption of 2,4-dinitrotoluene (DNT) from water are reported in Table 18. Both methanol and acetone were used as regenerants. Since methanol did not regenerate Ambersorb XE-340 as efficiently as acetone, methanol regeneration of the other carbonaceous adsorbents was not performed. Both solvents completely regenerated the polymeric adsorbents. Batch results for the polymerics agree to within 10 ± 3% of the capacities predicted by extrapolation of the linear isotherm lines to 180 ppm. Extrapolation works here because the concentration range is smaller than in previous studies. Amberlite XAD-4 has the highest regenerated saturation capacity. As observed in the PDC study, although isotherm data predict that Ambersorb XE-348 has a significantly higher capacity than Ambersorb XE-340, again, their regenerated capacities are essentially identical.

Both Amberlite XAD-4, a polymeric adsorbent, and Ambersorb XE-340, a carbonaceous adsorbent, were subjected to the rate test method. Rate test results are recorded in Tables 19 and 20 for XAD-4 and XE-340 respectively. Data are plotted in Figure 14. A linear regression analysis of each data set yields adsorption rates of 4.58 mg/g-min for XAD-4 and 0.82 mg/g-min for XE-340. XAD-4 approaches its equilibrium capacity at a much faster rate than XE-340. After one hour of exposure to the 180 ppm DNT stream, XAD-4 has reached 60% of its capacity while XE-340 has reached only 33% of its capacity. Repetition of the rate test with XE-340 yielded the same results. The slower adsorption rate for XE-340 is attributable to both its smaller surface area and its pore size distribution in macropores and micropores.[4]

Synthetic, Nitroaromatic Stream

A 4-component, synthetic, nitroaromatic stream was prepared with the following compounds: toluene (T), nitrobenzene (NB), 2-nitrophenol (NPL),

TABLE 16

ADSORPTION CAPACITIES FOR 1,2-DICHLOROPROPANE MEASURED BY BATCH TESTS[a]

Adsorbent	Methanol Regenerated Adsorption Capacity (mg/g)	Acetone Regenerated Adsorption Capacity (mg/g)
HP-20	1080	1030
XAD-4	1060	1090
XAD-7	543	584
XE-340	245	227
XE-348	222	220
FS-400	452	434

[a] 1,2-Dichloropropane concentration was maintained at 2450 ± 100 ppm.

TABLE 17

RATE TEST RESULTS FOR ADSORPTION OF 1,2-DICHLOROPROPANE BY XAD-4[a]

Time (min.)	Acetone Regenerated Adsorption Capacity (mg/g)	$\left(\frac{\text{Capacity, Time} = T}{\text{Equilibrium Capacity}}\right) \times 100$
13	531	48.7
20	607	55.7
27	693	63.6
35	740	67.9
50	750	68.8
66	756	69.4
99	849	77.9
180	927	85.0
1440	1010	92.7
2880	1090	100.0

[a] 1,2-Dichloropropane concentration was maintained at 2500 ± 100 ppm.

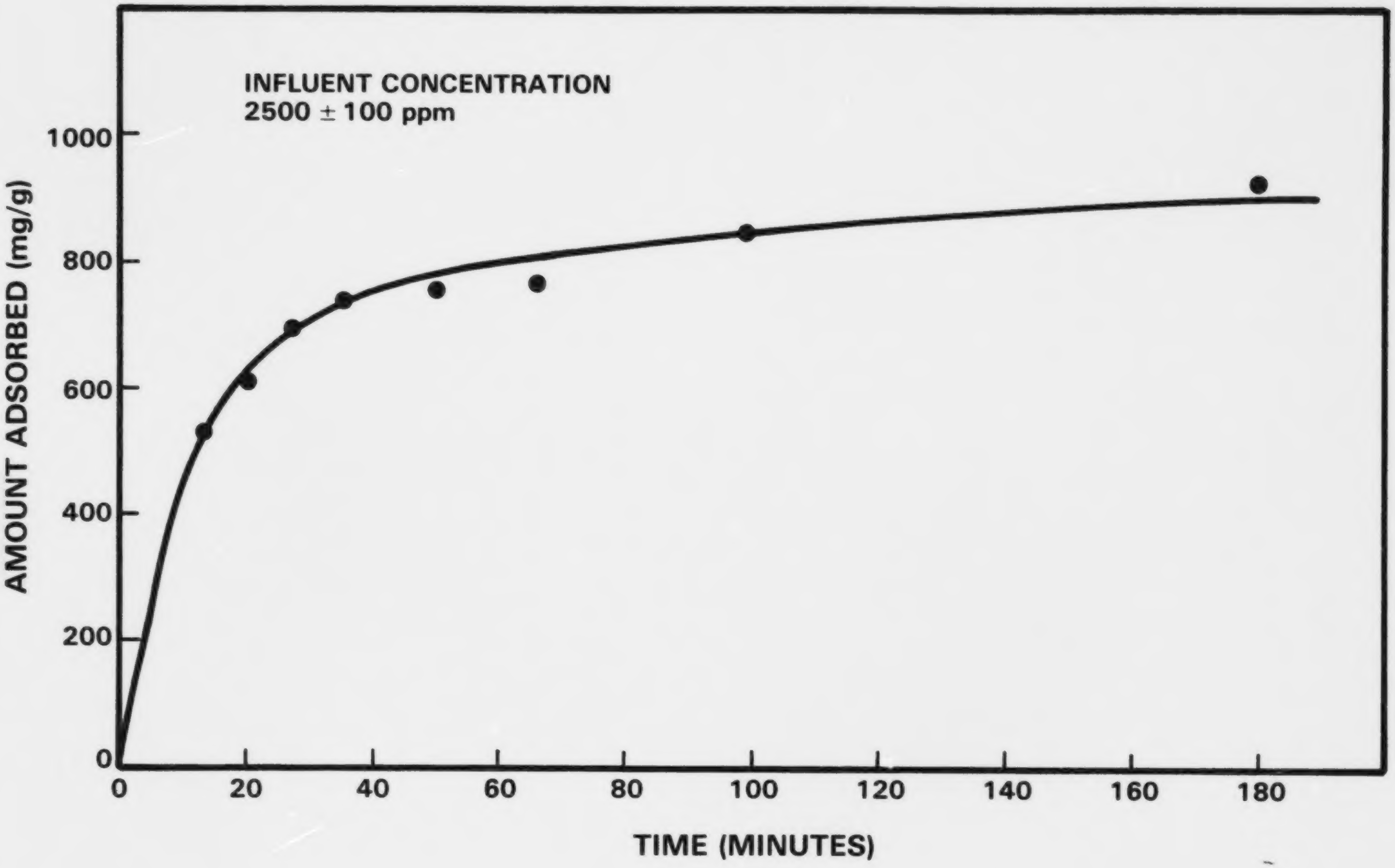


FIGURE 13. RATE OF ADSORPTION OF 1,2-DICHLOROPROPANE BY AMBERLITE XAD-4

TABLE 18

ADSORPTION CAPACITIES FOR 2,4-DINITROTOLUENE MEASURED BY BATCH TESTS[a]

Adsorbent	Methanol Regenerated Adsorption Capacity (mg/g)	Acetone Regenerated Adsorption Capacity (mg/g)
HP-20	363	362
XAD-4	460	440
XAD-7	287	285
XE-340	98	138
XE-348	-	133
FS-400	-	324

[a] 2,4-Dinitrotoluene concentration was maintained at 180 ± 10 ppm.

TABLE 19

RATE TEST RESULTS FOR ADSORPTION OF 2,4-DINITROTOLUENE BY XAD-4[a]

Time (min.)	Acetone Regenerated Adsorption Capacity (mg/g)	$\left(\frac{\text{Capacity, Time = T}}{\text{Equilibrium Capacity}}\right) \times 100$
8	58	12.9
14	96	21.3
24	178	39.6
40	239	53.1
55	271	60.2

[a] 2,4-Dinitrotoluene concentration was maintained at 175 ± 10 ppm.

TABLE 20

RATE TEST RESULTS FOR ADSORPTION OF 2,4-DINITROTOLUENE BY XE-340[a]

Time (min.)	Acetone Regenerated Adsorption Capacity (mg/g)	$\left(\frac{\text{Capacity, Time = T}}{\text{Equilibrium Capacity}}\right) \times 100$
12	14	10.1
24	23	16.7
39	37	26.8
52	46	33.3

[a] 2,4-Dinitrotoluene concentration was maintained at 175 ± 10 ppm.

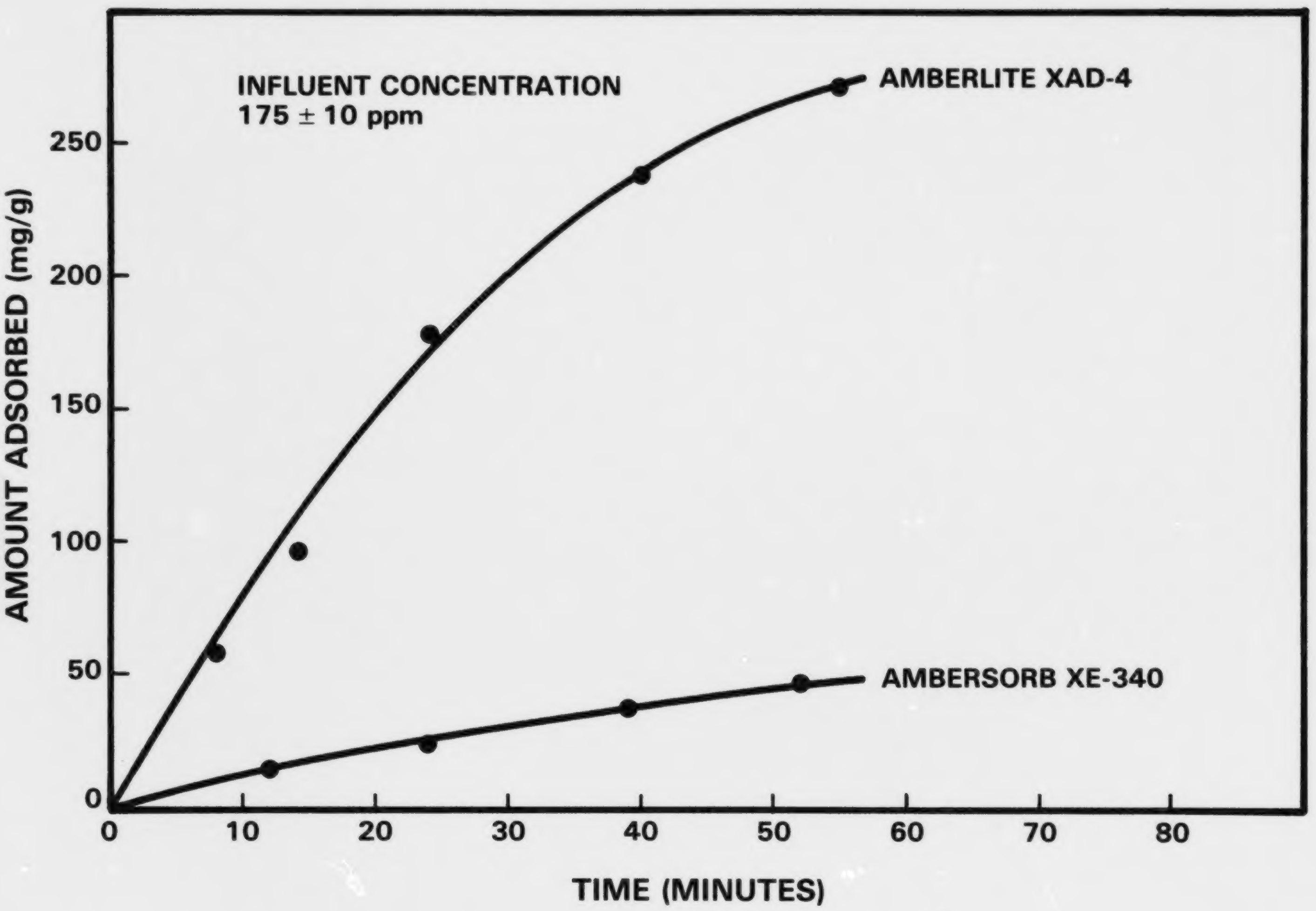


FIGURE 14. RATE OF ADSORPTION OF 2,4-DINITROTOLUENE

and 2,4-dinitrotoluene (DNT). These components were chosen for several reasons: availability of data obtained from testing these compounds individually (vide supra), similarity to more complex industrial waste streams such as those resulting from production of nitroaromatics or aromatic isocyanates [12,13], and reasonable ease of analysis using a Tenax GC column. Because pH changes influence resin adsorption [6,10,14] and alter chromatographic sensitivity, the stream was buffered with a pH 2 HCl/KCl buffer.

The nitroaromatic stream was established and maintained using the column method described in the Experimental Section. Three 70 g portions of Amberlite XAD-2 were loaded on approximately a gram per gram basis with one of the nitro compounds. 50 g of each solid (i.e. NPL and DNT) were slurried in 20 mL of toluene prior to mixing with an aqueous XAD-2 suspension. 70 g of liquid NB were added directly to an XAD-2 suspension. After a week of agitation on a platform rocker, each sample was batch washed to remove any excess organic which had not been adsorbed. The three portions of resin were then mixed and equilibrated prior to use in the column. Buffer was added to the 5 L reservoir and recirculated through the column to establish an equilibrated waste stream. This stream contained approximately 240 ppm T, 710 ppm NB, 510 ppm NPL, and 50 ppm DNT, or a cumulative organic concentration of 1510 ppm.

The results of batch test adsorption of this nitroaromatic stream are reported in Table 21. Samples of each saturated adsorbent were regenerated with acetone. The adsorbent with the highest regenerated saturation capacities for all components of this stream is Amberlite XAD-4. Diaion HP-20 also performs well. The cumulative adsorption capacities for XAD-4 and HP-20 are 1191 mg/g and 1105 mg/g respectively. The relative amounts of each species adsorbed by these polymeric adsorbents parallel their relative concentrations in the waste stream (i.e. DNT < T < NPL < NB).

The polymeric adsorbents HP-20 and XAD-4 and the carbonaceous adsorbent Ambersorb XE-340 were used in the rate studies. Results for HP-20 are recorded in Table 22 and plotted in Figure 15. Results for XAD-4 and XE-340 are recorded in Tables 23 and 24 and plotted in Figures 16 and 17 respectively. For all three resins, rate of approach to saturation is rapid. They attain 75% of their cumulative saturation capacities within 90 minutes. These adsorption rates exceed those measured in the single component studies.

As explained in the Introduction, resin adsorption of any given compound is influenced by a variety of factors including pH, dissolved electrolytes, and competition between adsorbable species. In the multicomponent stream, the added electrolyte (buffer) and other organic compounds decrease the solubility of each individual component and increase the component's adsorbability. Previous studies have shown that the presence of electrolytes increases the adsorptive capacity of XAD-4 for any given organic[14]. In Table 25, batch/rate data obtained for adsorption of NB, NPL, and DNT from the single component streams are compared to that obtained in the multicomponent stream. Both the linear equilibrium constants (i.e. batch equilibrium capacities corrected for pollutant

TABLE 21

ADSORPTION CAPACITIES FOR COMPONENTS OF THE SYNTHETIC, NITROAROMATIC STREAM MEASURED BY BATCH TESTS[a]

	Acetone Regenerated Capacity for (mg/g):			
Adsorbent	Toluene	Nitrobenzene	2-Nitrophenol	2,4-Dinitrotoluene
HP-10	155	463	241	107
HP-20	178	525	276	126
XAD-4	183	575	292	141
XAD-7	100	362	210	100
XE-340	37	131	72	46
XE-348	18	112	78	32

[a] Waste stream concentration was maintained at the following levels: toluene, 239 ± 12 ppm; nitrobenzene, 708 ± 35 ppm; 2-nitrophenol, 506 ± 25 ppm; 2,4-dinitrotoluene, 48 ± 3 ppm.

TABLE 22

RATE TEST RESULTS FOR ADSORPTION OF THE COMPONENTS OF THE SYNTHETIC, NITROAROMATIC STREAM BY HP-20[a]

	Acetone Regenerated Capacity for (mg/g):			
Time (min.)	Toluene	Nitrobenzene	2-Nitrophenol	2,4-Dinitrotoluene
10	79	289	153	32
18	97	331	167	46
30	112	343	171	62
47	126	354	173	69
80	128	363	180	75

[a] See Table 21 for waste stream concentrations.

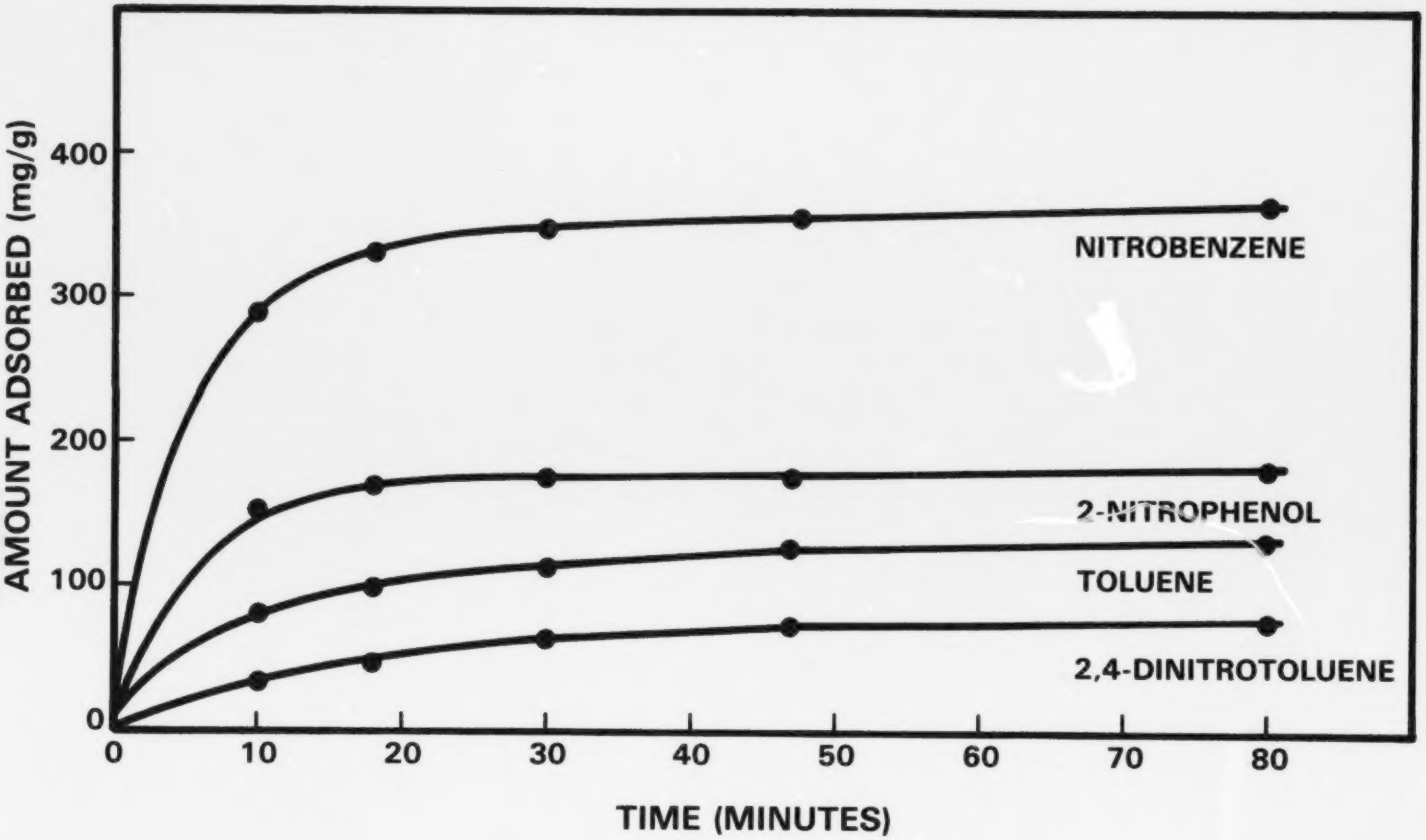


FIGURE 15. RATE OF ADSORPTION OF COMPONENTS OF THE NITROAROMATIC STREAM BY DIAION HP-20

TABLE 23

RATE TEST RESULTS FOR ADSORPTION OF THE COMPONENTS OF THE SYNTHETIC, NITROAROMATIC STREAM BY XAD-4[a]

	Acetone Regenerated Capacity for (mg/g):			
Time (min.)	Toluene	Nitrobenzene	2-Nitrophenol	2,4-Dinitrotoluene
10	59	287	152	22
15	92	363	186	35
25.5	114	428	208	54
31	126	436	217	59
55	137	452	218	74
87	131	453	222	82

[a] See Table 21 for waste stream concentrations.

TABLE 24

RATE TEST RESULTS FOR ADSORPTION OF THE COMPONENTS OF THE SYNTHETIC, NITROAROMATIC STREAM BY XE-340[a]

	Acetone Regenerated Capacity for (mg/g):			
Time (min.)	Toluene	Nitrobenzene	2-Nitrophenol	2,4-Dinitrotoluene
15	11	51	31	6
31	17	77	46	12
45	20	90	54	15
85	26	105	59	23
170	28	110	61	31

[a] See Table 21 for waste stream concentrations.

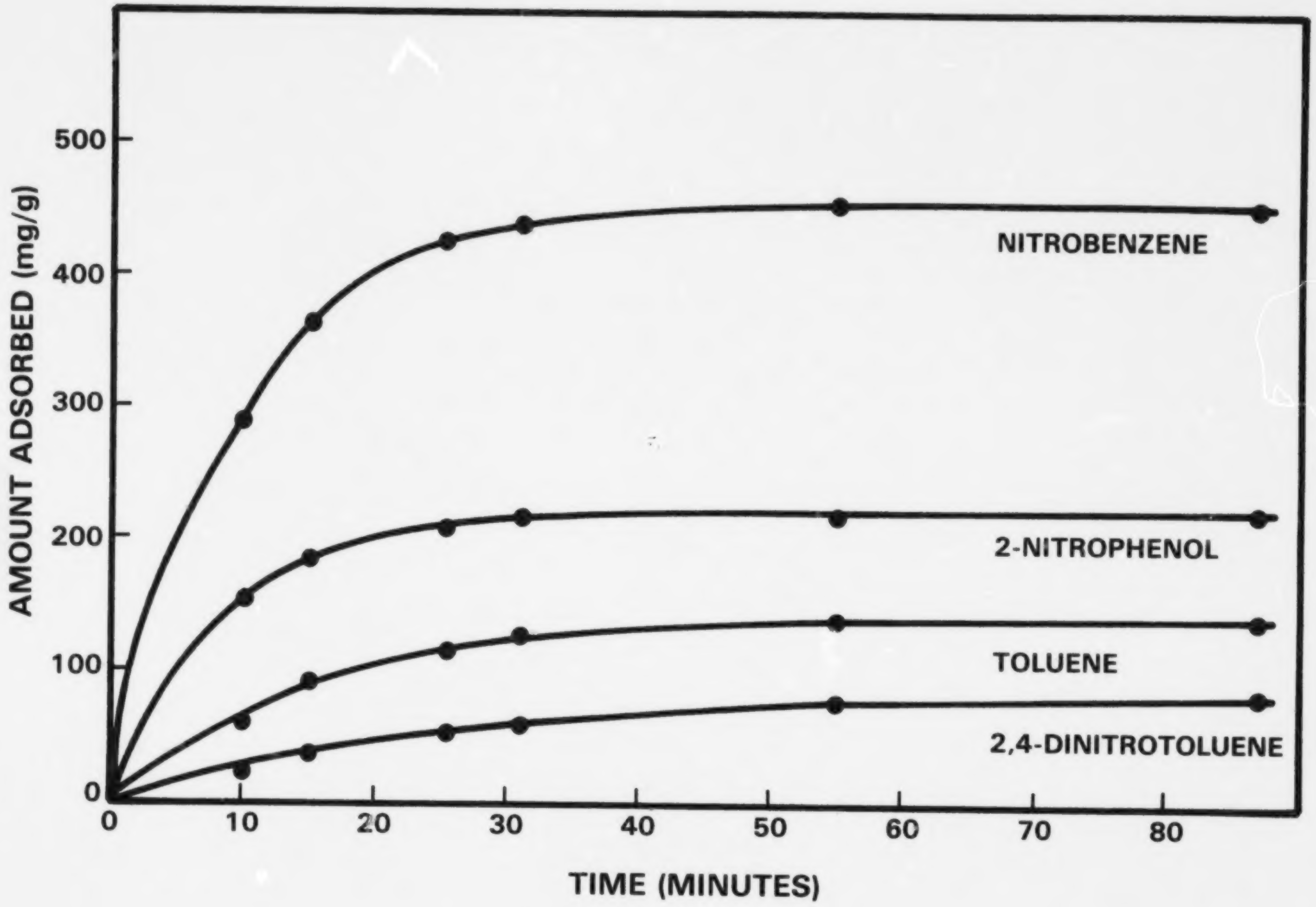


FIGURE 16. RATE OF ADSORPTION OF COMPONENTS OF THE NITROAROMATIC STREAM BY AMBERLITE XAD-4

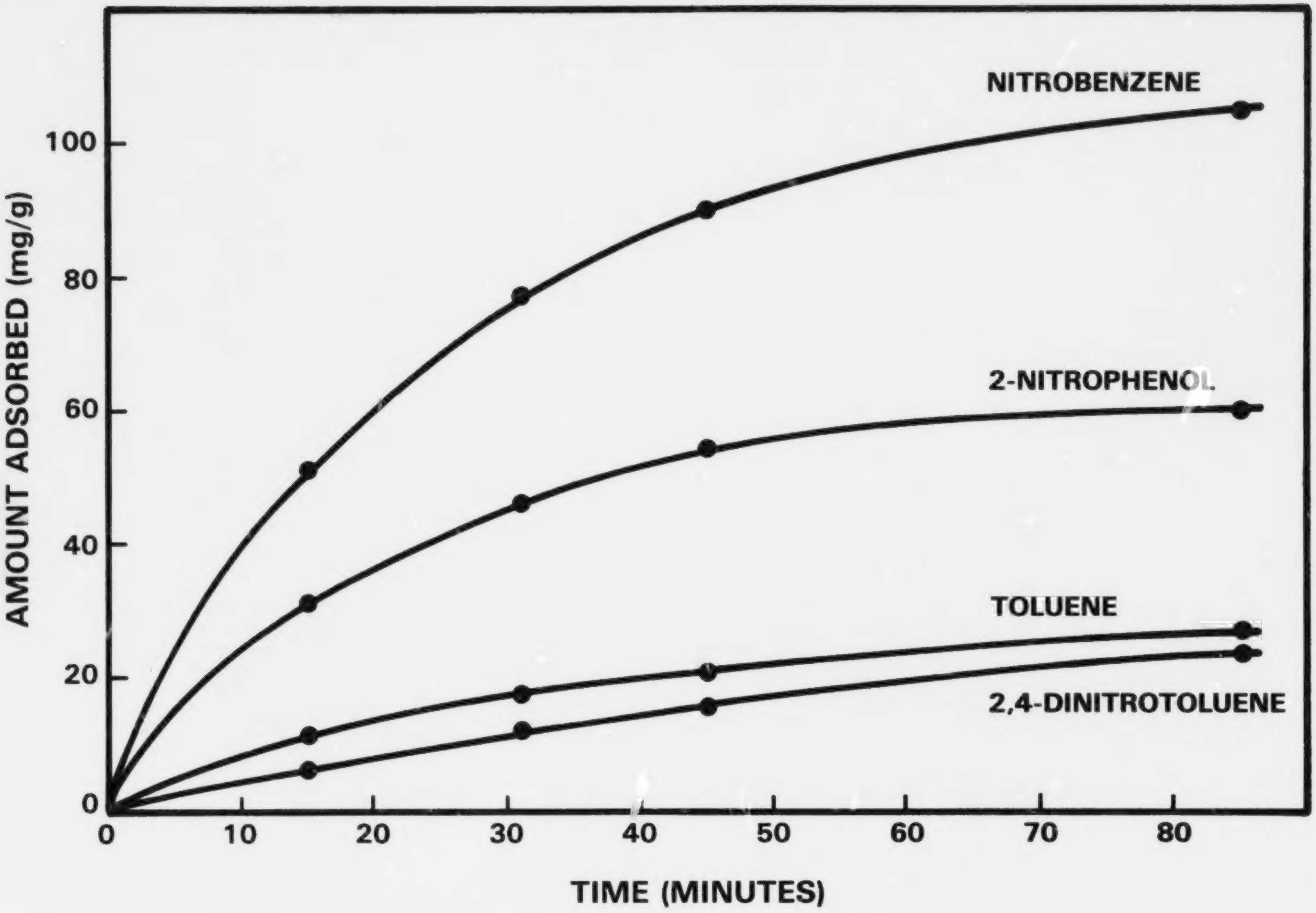


FIGURE 17. RATE OF ADSORPTION OF COMPONENTS OF THE NITROAROMATIC STREAM BY AMBERSORB XE-340

TABLE 25

COMPARISON OF BATCH/RATE DATA FROM STUDIES OF MULTICOMPONENT AND SINGLE COMPONENT NITROAROMATIC STREAMS

Linear Equilibrium Constants: Batch Capacity/Concentration (L/g)

Adsorbent	Stream	Nitrobenzene	2-Nitrophenol	2,4-Dinitrotoluene
XAD-4	Multi	0.81	0.58	2.94
XAD-4	Single	0.69	0.69	2.50
HP-20	Multi	0.74	0.55	2.63
HP-20	Single	0.61	NA[a]	2.02
XE-340	Multi	0.19	0.14	0.96
XE-340	Single	0.15	0.25	0.77

Mass Transfer Coefficients: Adsorption Rate/Concentration (L/g-min)

Adsorbent	Stream	Nitrobenzene	2-Nitrophenol	2,4-Dinitrotoluene
XAD-4	Multi	0.0097	0.0057	0.037
XAD-4	Single	0.0017	0.0054	0.025
HP-20	Multi	0.0036	0.0017	0.031
HP-20	Single	NA	NA	NA
XE-340	Multi	0.0019	0.0015	0.0063
XE-340	Single	NA	NA	0.0047

[a] NA = not available, required test not performed.

concentration) and the mass transfer coefficients (i.e. adsorption rates corrected for pollutant concentration) for NB and DNT are greater when adsorption occurs in the multicomponent stream. Although NPL data are also presented, comparison of adsorption data from the multi and single component streams is not valid because batch/rate testing of the pure NPL stream was done under different experimental conditions than all other batch/rate studies (*vide supra*).

Glen Cove Groundwater

Batch/rate testing using Ambersorb XE-340 was done on a contaminated groundwater source in Glen Cove, NY. In an EPA funded pilot plant study performed by the firm of Nebolsine Kohlman Ruggiero Engineers, Glen Cove City well water was successfully treated with Ambersorb XE-340 for removal of chlorinated organics[15]. The removal of cis-1,2-dichloroethylene (CIS), trichloroethylene (TRI), tetrachloroethylene (TETRA), and 1,1,1-trichloroethane (ETH) by several treatment technologies was studied. Batch/rate testing of this water assesses the ability of the new test procedure to predict resin performance in very dilute streams (1 ppm total organics). The results of batch/rate testing may be compared to and correlated with column results from the pilot plant study (Appendix E).

During the batch/rate testing period the average pollutant concentrations were 80 ppb CIS, 190 ppb TRI, 40 ppb TETRA, and 5 ppb ETH. A reservoir (a 55 gal pail) was established at the stream source (a pipe) and water continually cascaded into the reservoir. Compared to previous batch/rate tests, larger "tea bags" (100 sq in) and more adsorbent (25 g) were used for each sample to facilitate examination of both steam and solvent regeneration. Because pollutant concentrations were so low compared to others used during this project, exposure times had to be significantly increased.

The results of acetone regeneration of rate test samples exposed to the groundwater from 1 to 215 hours are recorded in Table 26. Because ETH contributes less than 2% of the total organic load, it is not included here. The data from samples obtained during the first 48 hours are plotted in Figure 18. Linear regression analysis of these data yield the following adsorption rates: CIS-10.2 μg/g-hr, TRI-25.7 μg/g-hr, and TETRA-4.3 g/g-hr. The batch (equilibrium) sample, exposed to the stream for 1224 hours (51 days), was acetone regenerated to yield the following capacities: CIS-4810 μg/g, TRI-10,900 μg/g, and TETRA-2390 μg/g. Based on Glen Cove pilot plant column results (Table E-1), resin saturation has not been achieved. For example, at a flow of .5 BV/hr (4 gpm/ft^3), column capacities to 10% leakage are: CIS-2330 μg/g, TRI-30,800 μg/g, and TETRA-14,600 μg/g. Cumulative column capacity to 10% leakage is thus 47,700 μg/g as compared to a cumulative "batch" capacity of 18,100 μg/g. Since the batch test sample was not exposed long enough to achieve equilibrium, no prediction of column performance from batch/rate data can be made.

Steam regeneration of several XE-340 rate samples was performed according to the published procedure[2]. Approximately 40 mL (19 g) of

TABLE 26

RATE TEST RESULTS FOR ADSORPTION OF THE COMPONENTS OF THE GLEN COVE STREAM BY XE-340[a]

Time (hr.)	Acetone Regenerated Capacity for (μg/g): Cis-1,2-Dichloroethylene	Trichloroethylene	Tetrachloroethylene
1	9.7	27.8	4.1
2	20.2	22.4	9.7
2 3/4	29.5	82.9	10.8
11	129	339	54.0
25	217	786	129
48 1/4	504	1210	201
214 3/4	2742	5400	1170

[a] Average concentrations: cis-1,2-dichloroethylene, 80 ppb; trichloroethylene, 190 ppb; tetrachloroethylene, 40 ppb.

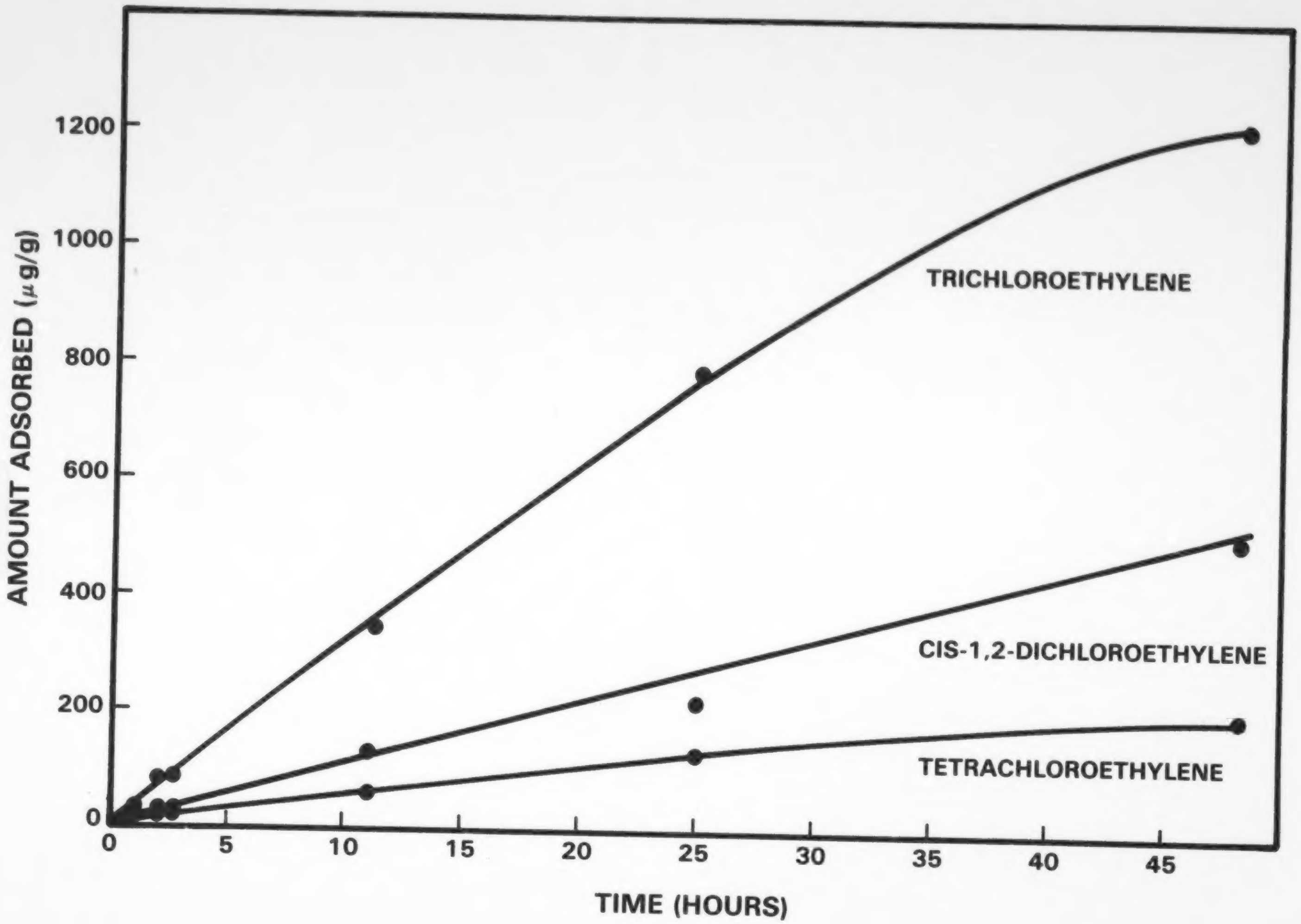


FIGURE 18. RATE OF ADSORPTION OF COMPONENTS OF THE GLEN COVE STREAM BY AMBERSORB XE-340

resin was steam regenerated at 1 BV/hr for 12 BV. Because resin loading was so low (Table 26) and total regenerant volume so high (~500 mL), resulting pollutant concentrations were very low. Per gram resin, about 25 mL condensed steam was used as compared to 10 mL acetone. The low concentrations and large number of fractions collected resulted in unsatisfactory steam regeneration data. For example, steam regeneration of the 11 hour rate sample yielded only 65% of the cumulative capacity as obtained by acetone regeneration. Similarly steam regenerated capacities were only 80% of the acetone regenerated capacities for the 25 hour rate sample. Despite the problems encountered here, steam regeneration of Ambersorb XE-340 used in Glen Cove groundwater treatment has been demonstrated previously [2,15].

COLUMN EXPERIMENTS

The general procedures for column loading and regeneration were described previously. Effluent concentration is measured as a function of the volume of solution passed through the column. Breakthrough curves are plotted as effluent concentration as percent of influent versus volume of treated solution. These curves are usually non-symmetrical and exhibit tailing as column saturation is approached. Saturation column capacity (mg/g) is determined by integration of the area above the breakthrough curve. Capacity can be estimated to 95 ± 5% directly from the graph by

$$\text{Saturation Column Capacity} = \frac{V_{60\%} \, C_I}{W_R}$$

where $V_{60\%}$ is volume treated to 60% breakthrough, C_I is influent concentration in mg/L, and W_R is grams of dry adsorbent.

For column regeneration, regeneration concentration is measured as a function of volume collected in 1/4 BV fractions. Regeneration curves are plotted as cumulative amount of pollutant regenerated per weight adsorbent versus bed volumes of regenerant. Column regeneration was complete in 3 BV or less. Since regenerated column capacity is the sum of 10 or more analyses, this measurement is subject to more experimental error than batch test data. Because of this experimental error, regenerated column capacity sometimes exceeds loaded column capacity. Nevertheless, the data for these three test methods agree very well in almost all cases.

The following operating variables have been found to be suitable for lab-scale column studies: 1) bed diameter of 11 mm and bed height of 110 mm, 2) flow rates of 8 and 16 BV/hr. Due to the high concentrations of wastes to be adsorbed, smaller beds and faster flows are likely to produce premature breakthrough.

2-Nitrophenol

Two columns of Amberlite XAD-4, one 12.0 mL BV and the other 24.0 mL BV, were loaded with 1080 ± 50 ppm aqueous NPL buffered at pH 5, at flow rates of 16 BV/hr and 8 BV/hr respectively. Breakthrough curves are shown in Figure 19. The saturation column capacity is 927 mg/g for the 12.0 mL BV column and 685 mg/g for the 24.0 mL BV column. Each column was regenerated with methanol as shown in Figure 20. The shorter column regenerated 739 mg/g and the longer column regenerated 847 mg/g. This discrepancy is primarily due to experimental procedures which were modified after the entire nitrophenol study was completed and the results of isotherm, batch/rate, and column experiments were compared. Thus NPL capacity data obtained by these three test methods do not correlate well.

The column performance of XAD-4 was similarly measured for removal of 1065 ± 50 ppm NPL from an aqueous stream buffered at pH 8. Breakthrough curves for the 12.0 mL and 24.0 mL columns which were loaded at 16 BV/hr and 8 BV/hr respectively, are displayed in Figure 21. Saturation column capacities are 282 mg/g and 299 mg/g respectively. Methanol regeneration of these columns (see Figure 22) resulted in regeneration capacities of 272 mg/g and 231 mg/g. Despite the similar saturation capacities of these two columns, the almost immediate breakthrough of NPL on the shorter column indicates that the 16 BV/hr flow rate is too rapid. As demonstrated previously by both isotherm and batch/rate testing, NPL adsorption by XAD-4 is much greater at lower pH where NPL exists in its neutral form.

Column adsorption of NPL by Amberlite XAD-8 was also examined. A 24.0 mL BV column and an 8 BV/hr flow rate were used. Two columns, one each at pH 5 and 8, were run to determine if NPL adsorption by an acrylic resin (XAD-8) was as pH sensitive as adsorption by polystyrene resin (XAD-4). The results of these column loading experiments are displayed in Figure 23. Saturation column capacity at pH 5 is 247 mg/g and at pH 8 is 124 mg/g. The methanol regenerated capacities of these columns are 332 mg/g and 82 mg/g respectively (see Figure 24). Results indicate that NPL adsorption by XAD-8 is significantly better at lower pH.

Nitrobenzene

Two columns of Amberlite XAD-4, one 11.0 mL BV and the other 23.1 mL BV, were loaded with 1805 ± 30 ppm aqueous NB at flow rates of 16 BV/hr and 8 BV/hr respectively. The results are plotted in Figure 25. The saturation column capacity is 1260 mg/g for the 11.0 mL BV column and 1330 mg/g for the 23.1 mL BV column. The results of methanol regeneration are shown in Figure 26. The 11.0 mL bed regenerated 1080 mg/g or 86% and the 23.1 mL bed regenerated 1250 mg/g or 94%. The column saturation capacity agrees well with the batch capacity of 1310 mg/g.

Similarly, a 11.6 mL BV column of Amberlite XAD-8 and a 24.3 mL BV column of Diaion HP-20 were loaded with aqueous NB at flows of 16 BV/hr and 8 BV/hr respectively. Breakthrough curves are plotted in Figure 27. The column capacity is 569 mg/g for XAD-8 and 1150 mg/g for HP-20. Results of methanol regeneration are presented in Figure 28. The XAD-8 column regenerated 530 mg/g or 93% and the HP-20 column regenerated 1090 mg/g or 95%. Again column results agree with the batch results of 580 mg/g for XAD-8 and 1160 mg/g for HP-20.

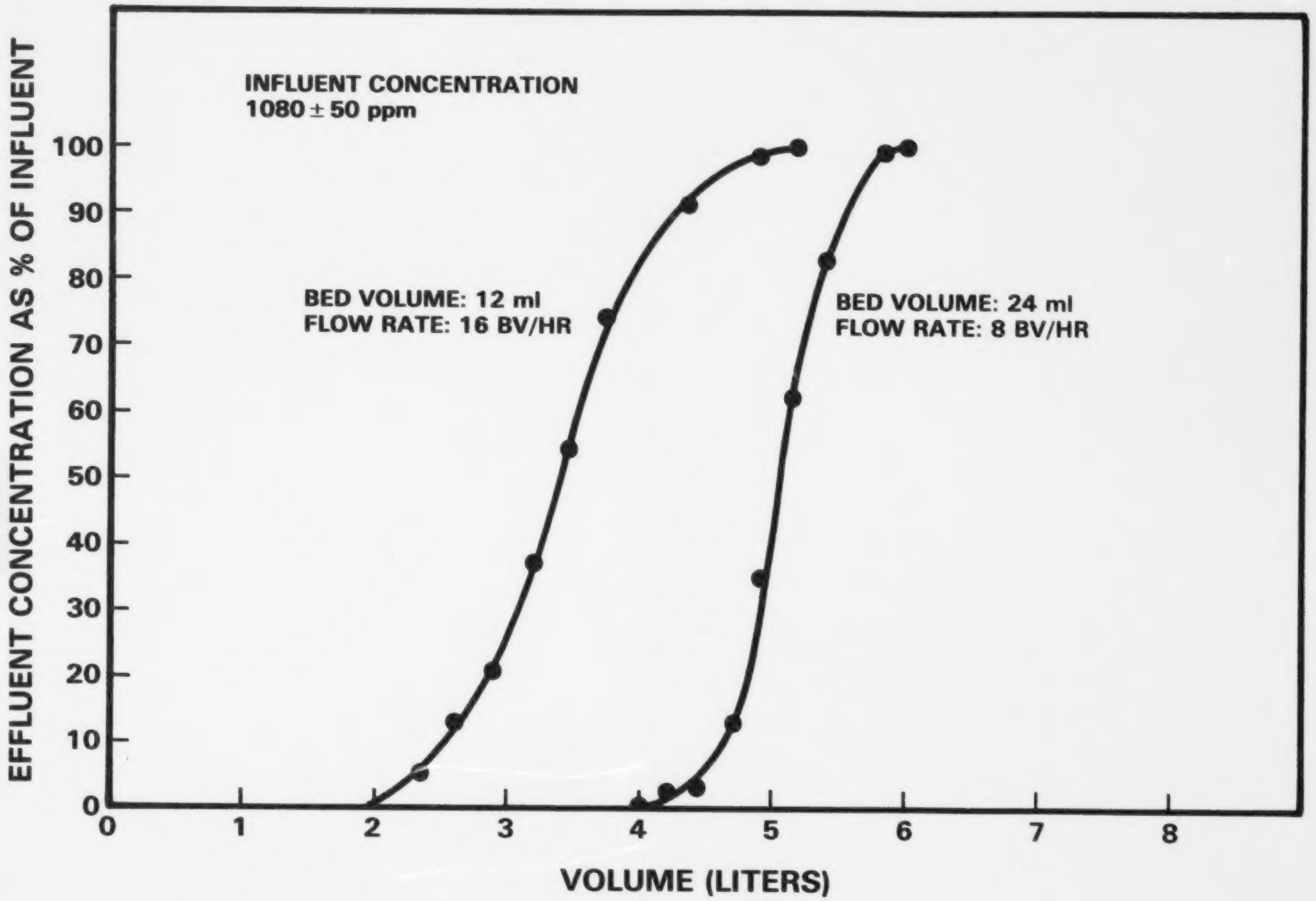


FIGURE 19. COLUMN ADSORPTION OF 2-NITROPHENOL (pH 5) BY AMBERLITE XAD-4

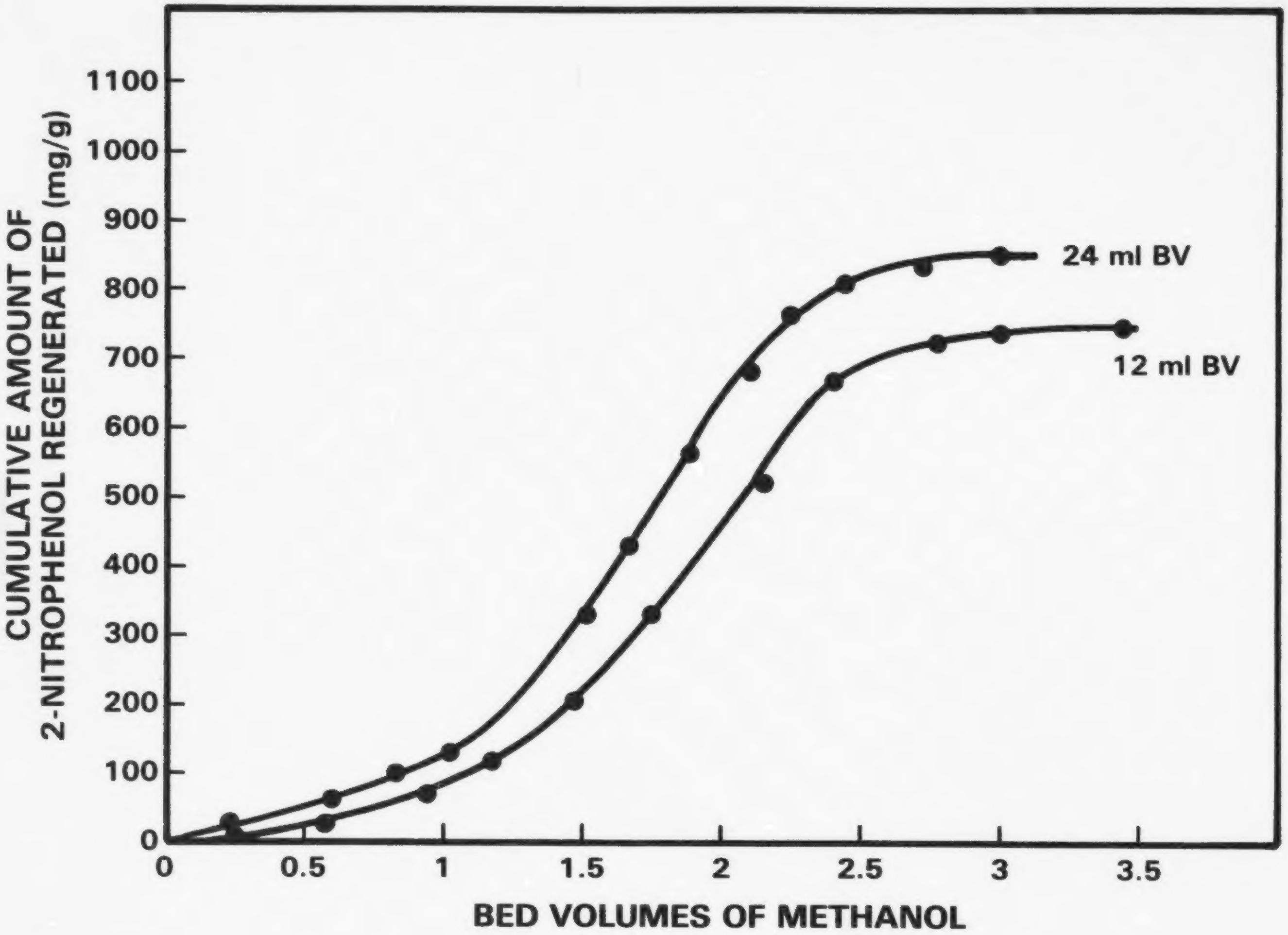


FIGURE 20. COLUMN REGENERATION OF 2-NITROPHENOL (pH 5) LOADED AMBERLITE XAD-4

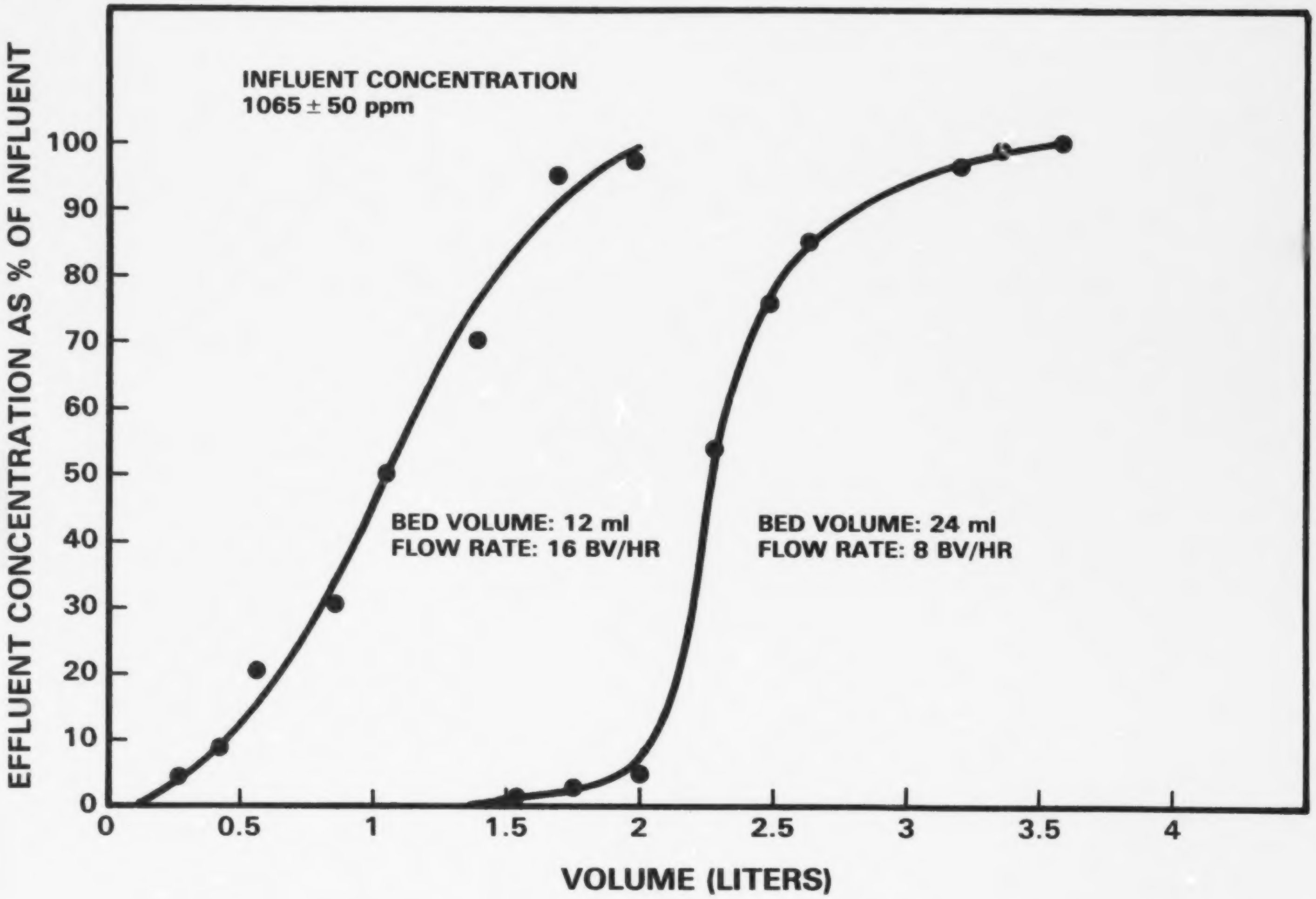


FIGURE 21. COLUMN ADSORPTION OF 2-NITROPHENOL (pH 8) BY AMBERLITE XAD-4

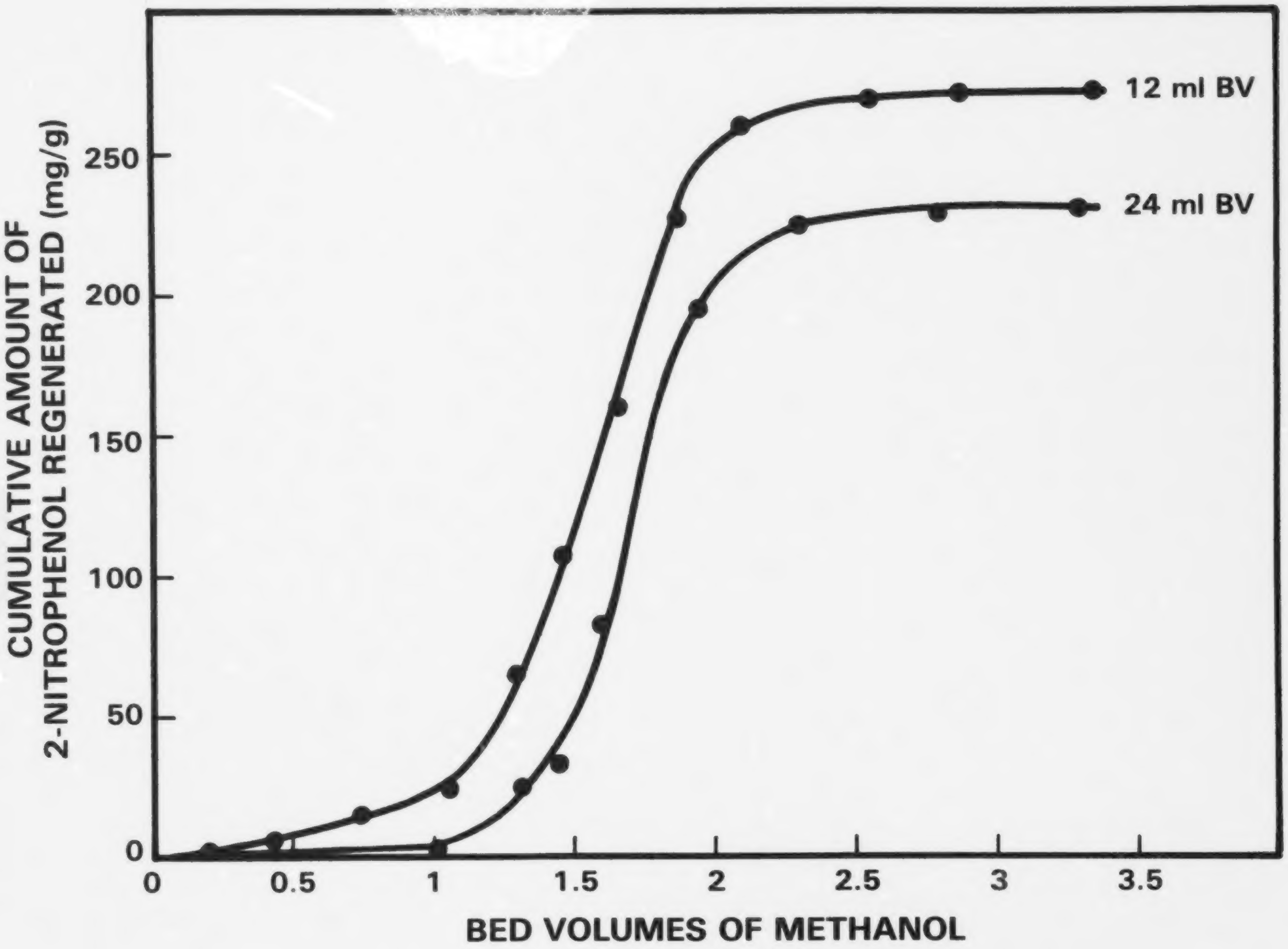


FIGURE 22. COLUMN REGENERATION OF 2-NITROPHENOL (pH 8) LOADED AMBERLITE XAD-4

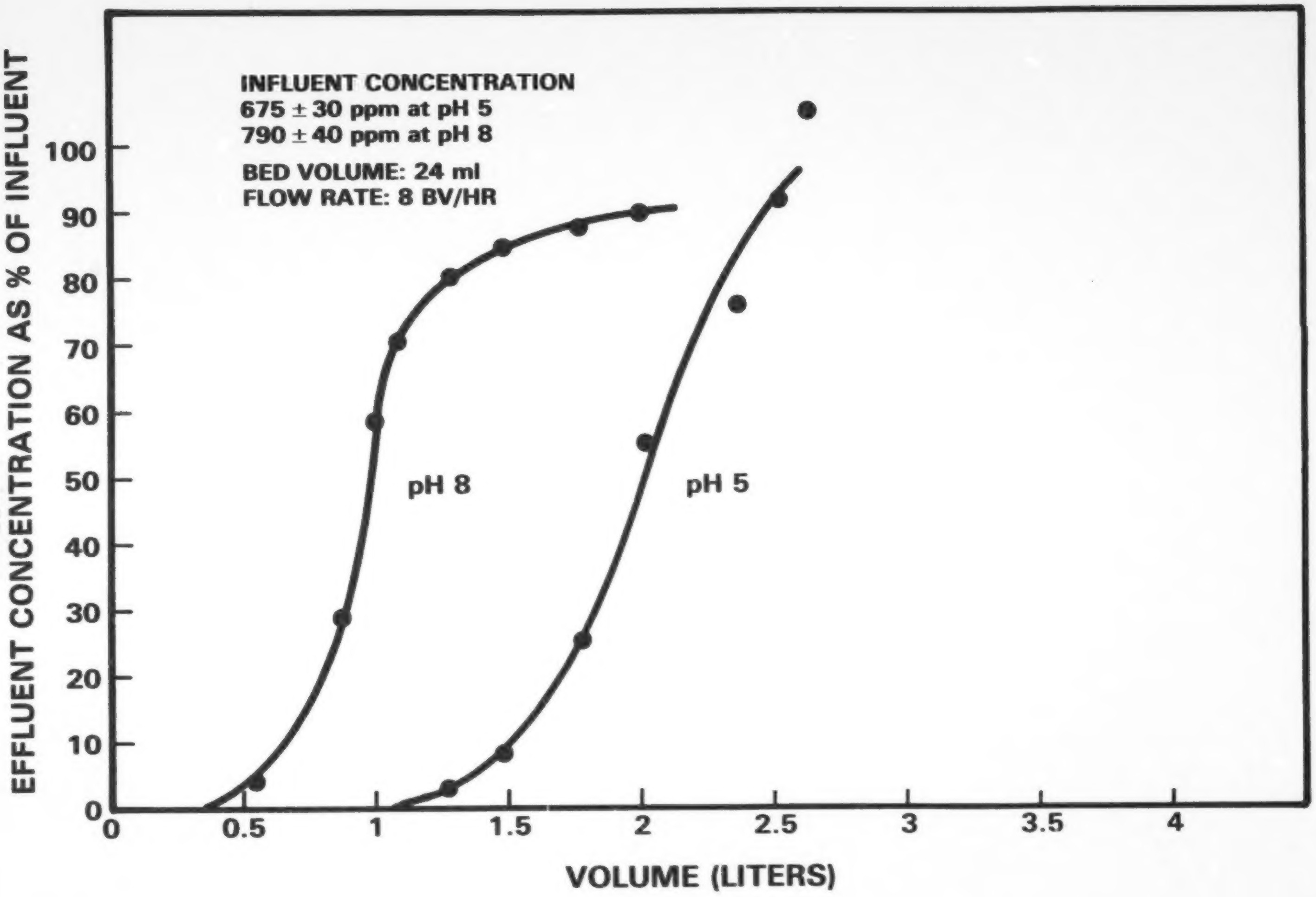


FIGURE 23. COLUMN ADSORPTION OF 2-NITROPHENOL BY AMBERLITE XAD-8

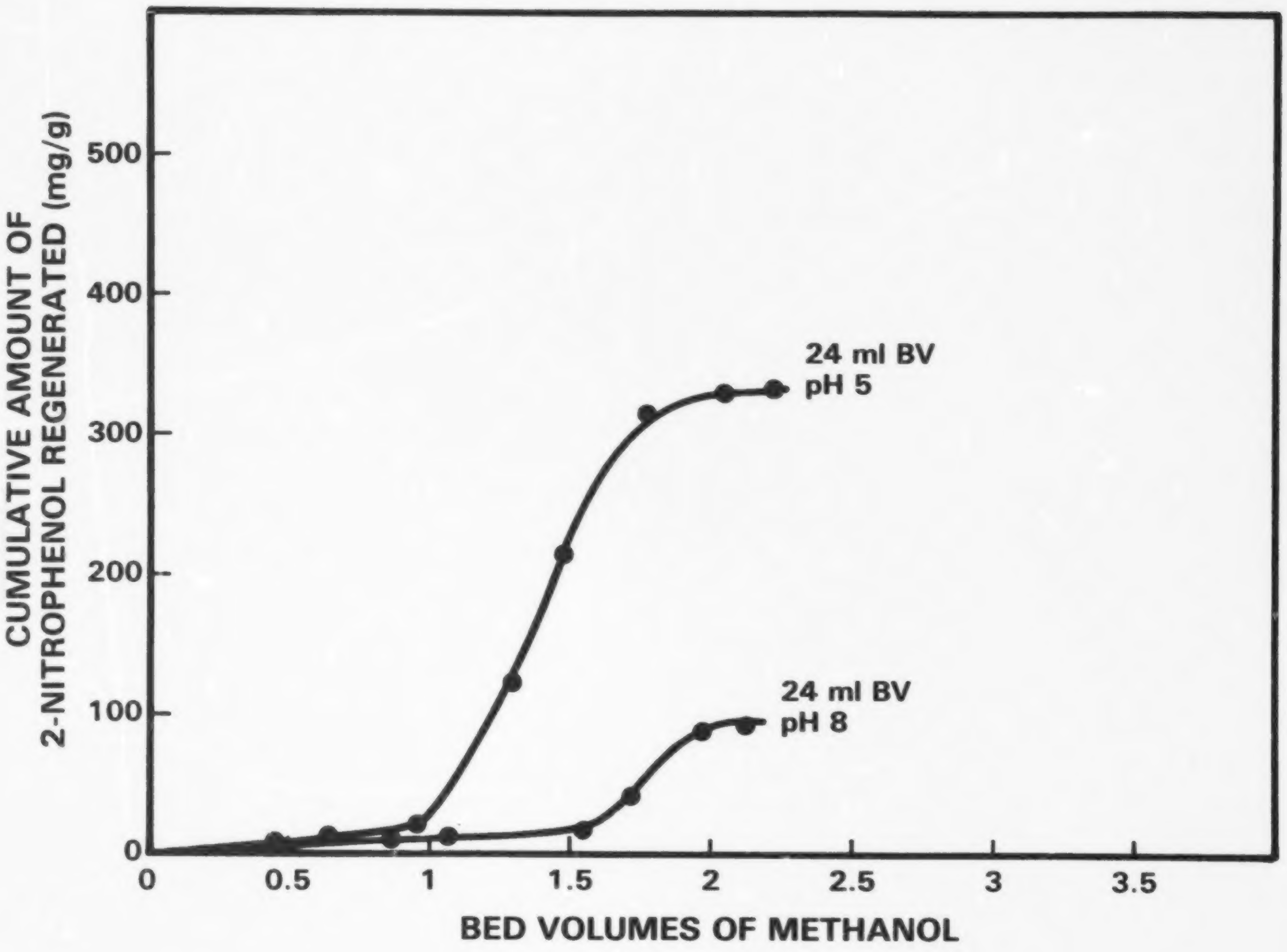


FIGURE 24. COLUMN REGENERATION OF 2-NITROPHENOL LOADED AMBERLITE XAD-8

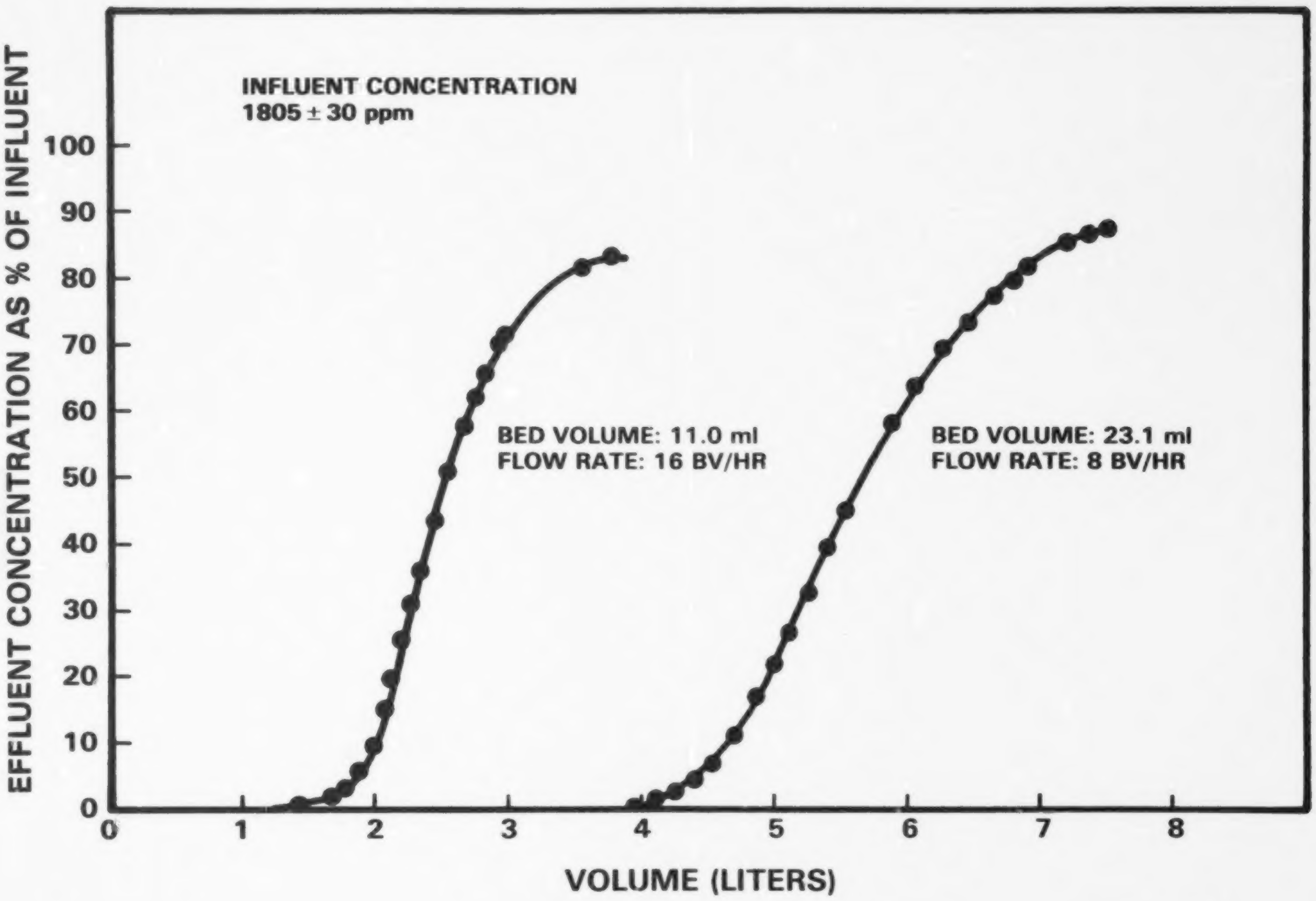


FIGURE 25. COLUMN ADSORPTION OF NITROBENZENE BY AMBERLITE XAD-4

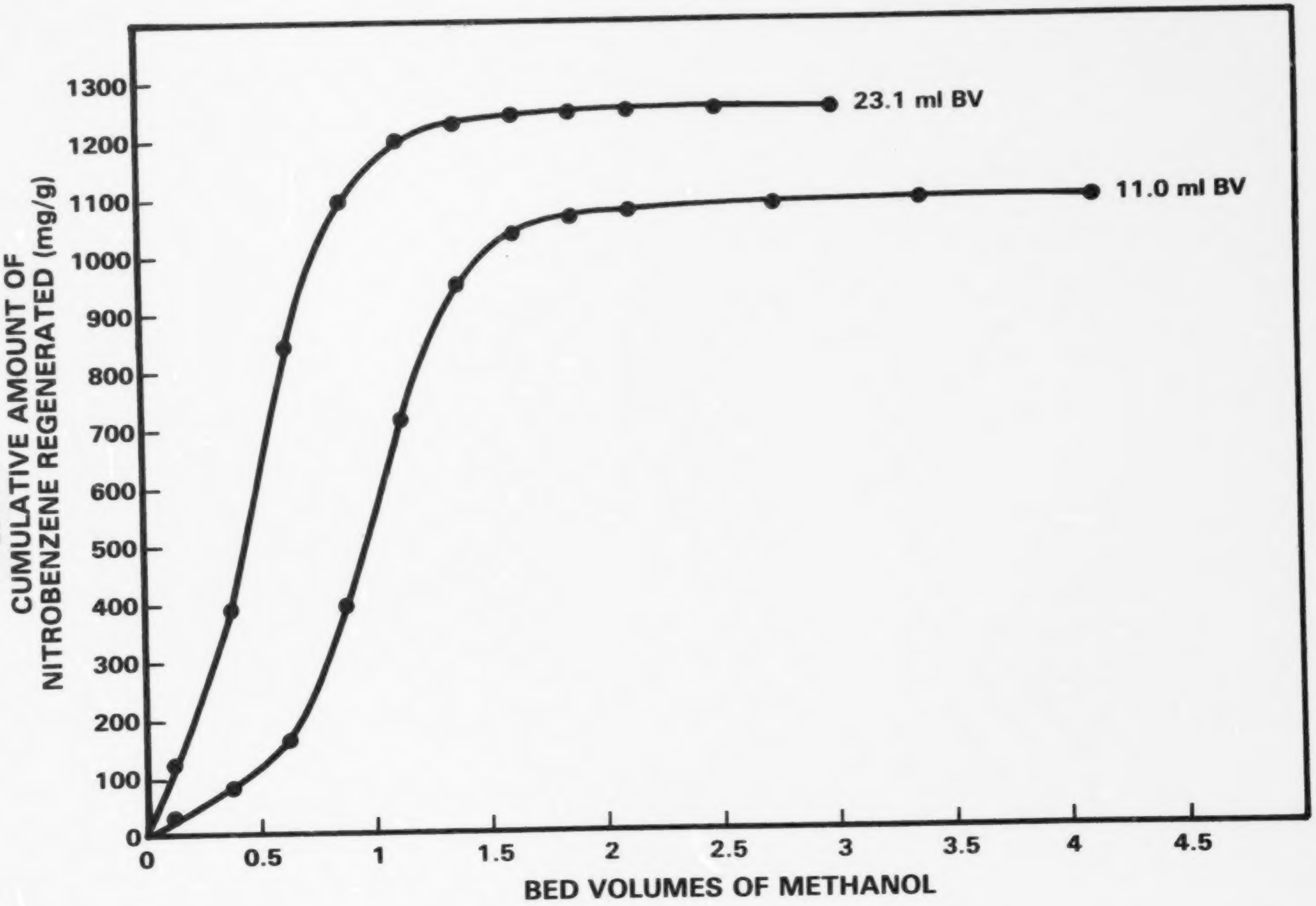


FIGURE 26. COLUMN REGENERATION OF NITROBENZENE LOADED AMBERLITE XAD-4

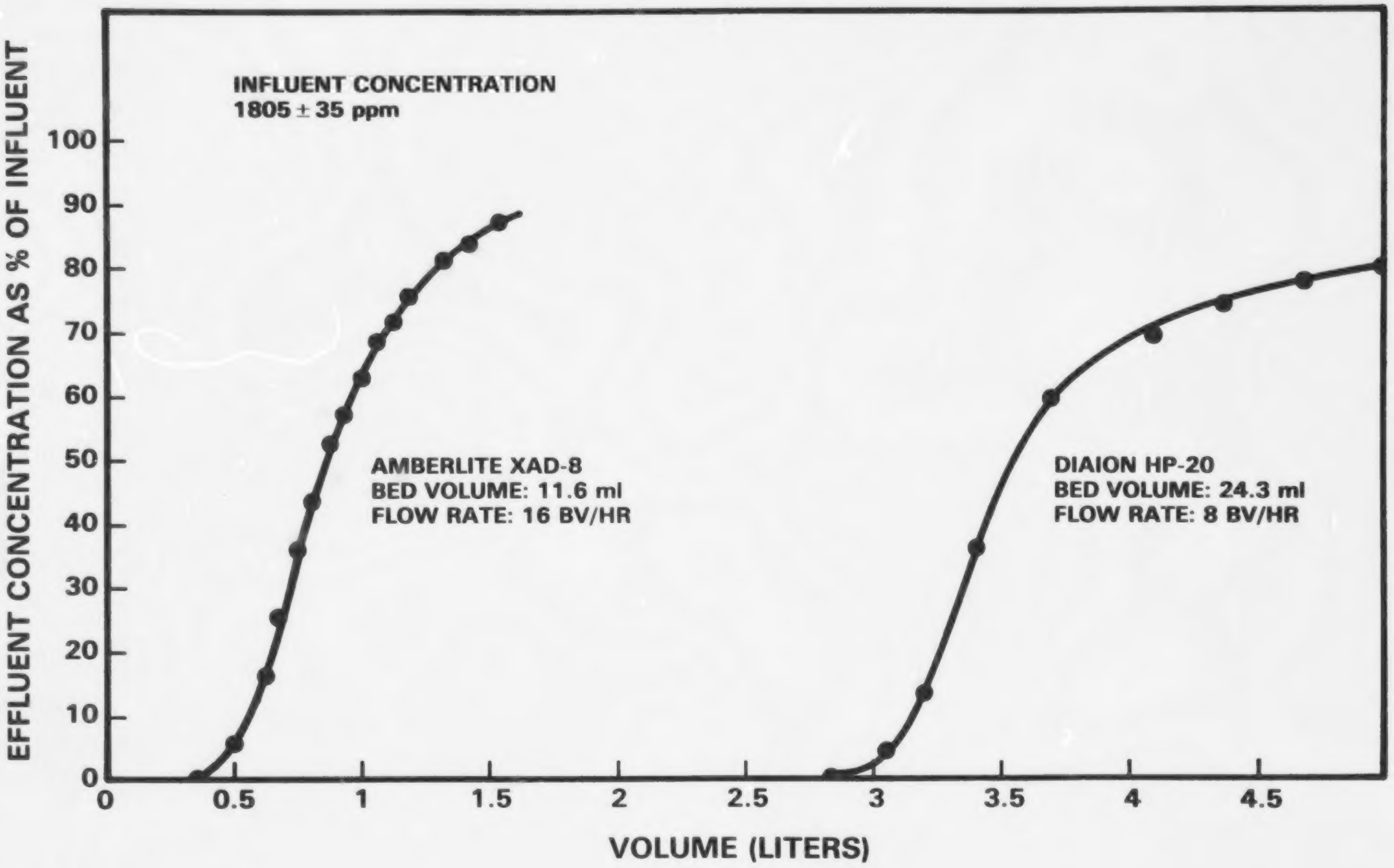


FIGURE 27. COLUMN ADSORPTION OF NITROBENZENE BY SELECTED ADSORBENTS

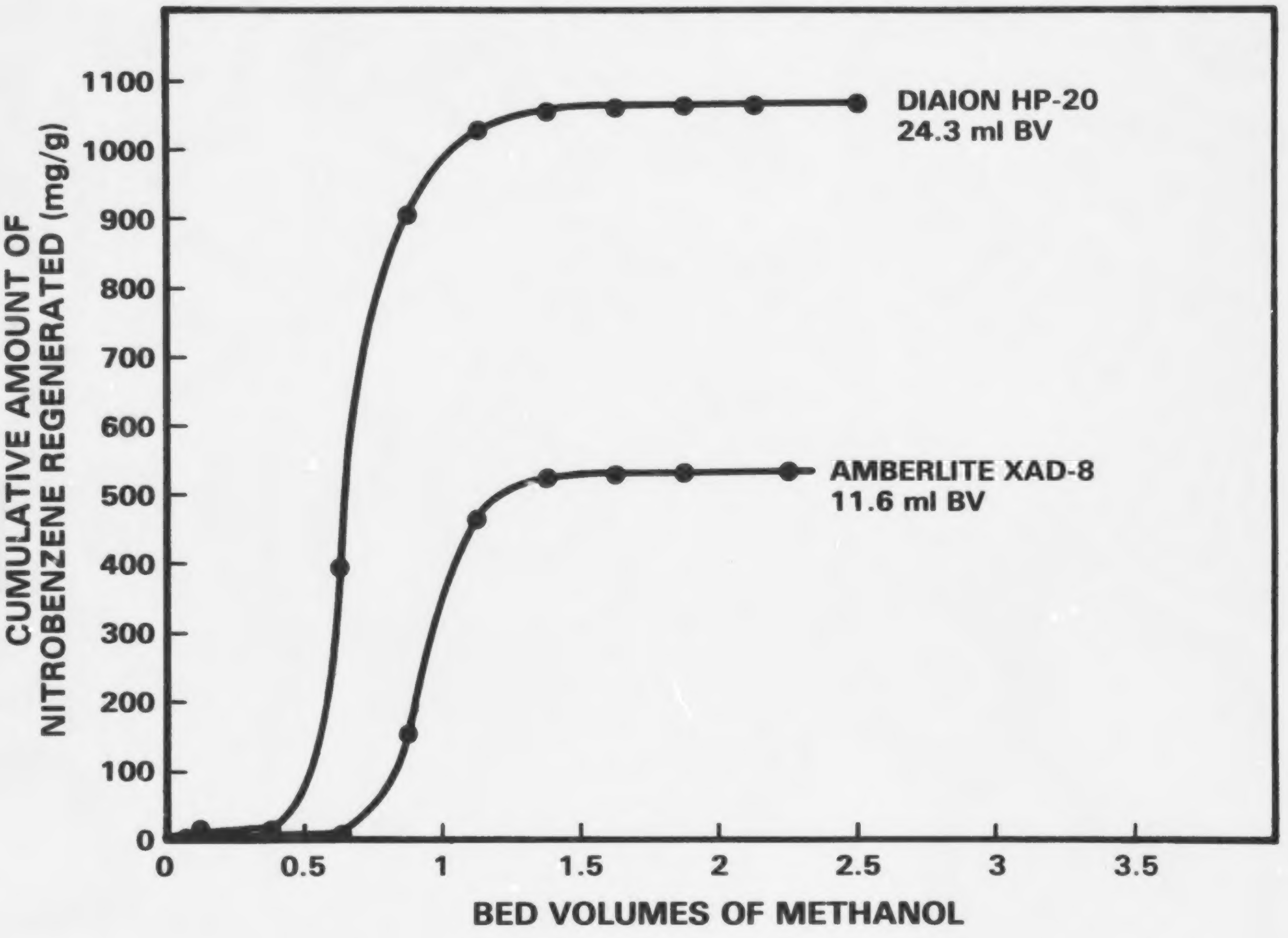


FIGURE 28. COLUMN REGENERATION OF NITROBENZENE LOADED ADSORBENTS

1,2-Dichloropropane

Both a 10.4 mL BV and a 23.9 mL BV column of Amberlite XAD-4 were loaded with 2350 ± 80 ppm aqueous PDC at flow rates of 16 BV/hr and 8 BV/hr respectively. Results are plotted in Figure 29. Integration of the area above each breakthrough curve yields saturation capacities of 1240 mg/g for the shorter column and 1310 mg/g for the longer column. In Figure 30, the results of acetone regeneration are shown. The 10.3 mL column regenerated 1160 mg/g or 94% and 23.9 mL column regenerated 1150 mg/g or 88%. Batch results predict a saturation capacity of 1090 mg/g.

An 11.7 mL BV column of Diaion HP-20 and a 27.1 mL BV column of Amberlite XAD-7 were loaded with aqueous PDC at flows of 16 BV/hr and 8 BV/hr respectively. The data, plotted in Figure 31, yield capacities of 1200 mg/g for HP-20 and 523 mg/g for XAD-7. Acetone regeneration results are shown in Figure 32. The HP-20 column regenerated 1030 mg/g or 86% and the XAD-7 column regenerated 544 mg/g or 104%. The cumulative total of PDC regenerated from the XAD-7 column appears to exceed the amount of PDC loaded. This discrepancy is due to the number of samples analyzed during regeneration (vide supra). The capacities agree well with those predicted by batch tests: 1055 mg/g for HP-20 and 564 mg/g for XAD-7.

2,4-Dinitrotoluene

To determine the effects of increased flow rates on column performance, two columns having similar bed volumes of Amberlite XAD-4 were loaded with 178 ± 10 ppm aqueous DNT. Thus, a 10.4 mL BV column was loaded at 16 BV/hr and a 11.4 mL BV column was loaded at 24 BV/hr. The breakthrough curves are displayed in Figure 33. Although saturation column capacities are identical for these two columns (i.e., 434 mg/g and 432 mg/g) the slower flow produced significantly better performance in the early portion of breakthrough. To 10% breakthrough (18 ppm DNT in the effluent) the 10.4 mL BV column had treated 6.4 L or 615 BV of solution while the 11.4 mL BV column had treated 5.6 L or 490 BV of solution. This is a 20% difference during initial DNT leakage. The results of acetone regeneration are plotted in Figure 34. The 10.4 mL BV column regenerated 470 mg/g and the 11.4 mL BV column regenerated 474 mg/g. These capacities are higher than the loaded capacities due to analytical problems which developed during the GC analysis of aqueous DNT solutions. The GC data for acetone solutions of DNT are quite reliable and calibration standards varied only ±5% during the entire DNT study. These saturation capacities agree well with the XAD-4 batch capacity of 450 mg/g.

To make it possible to correlate batch/rate data to column performance for carbonaceous adsorbents, a column study using Ambersorb XE-340 was undertaken. A 10.8 mL BV column of XE-340 was loaded with aqueous DNT at 16 BV/hr to 95% breakthrough. Column loading data are plotted in Figure 35; acetone regeneration data are shown in Figure 36. As predicted by batch testing, acetone fully regenerated the XE-340 column. The loaded capacity of 148 mg/g and the regenerated capacity of 151 mg/g agree satisfactorily with the batch capacity of 138 mg/g.

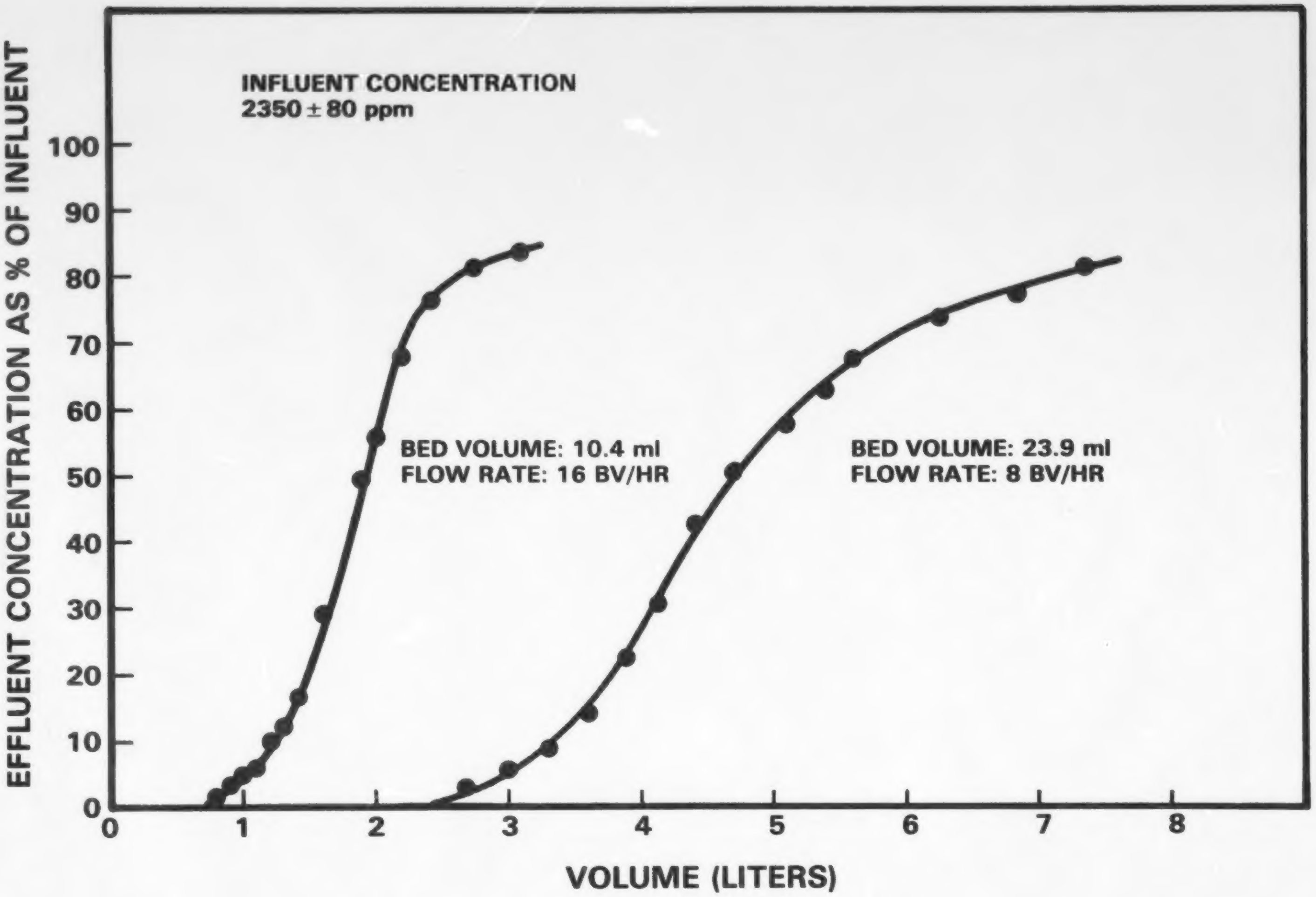


FIGURE 29. COLUMN ADSORPTION OF 1,2-DICHLOROPROPANE BY AMBERLITE XAD-4

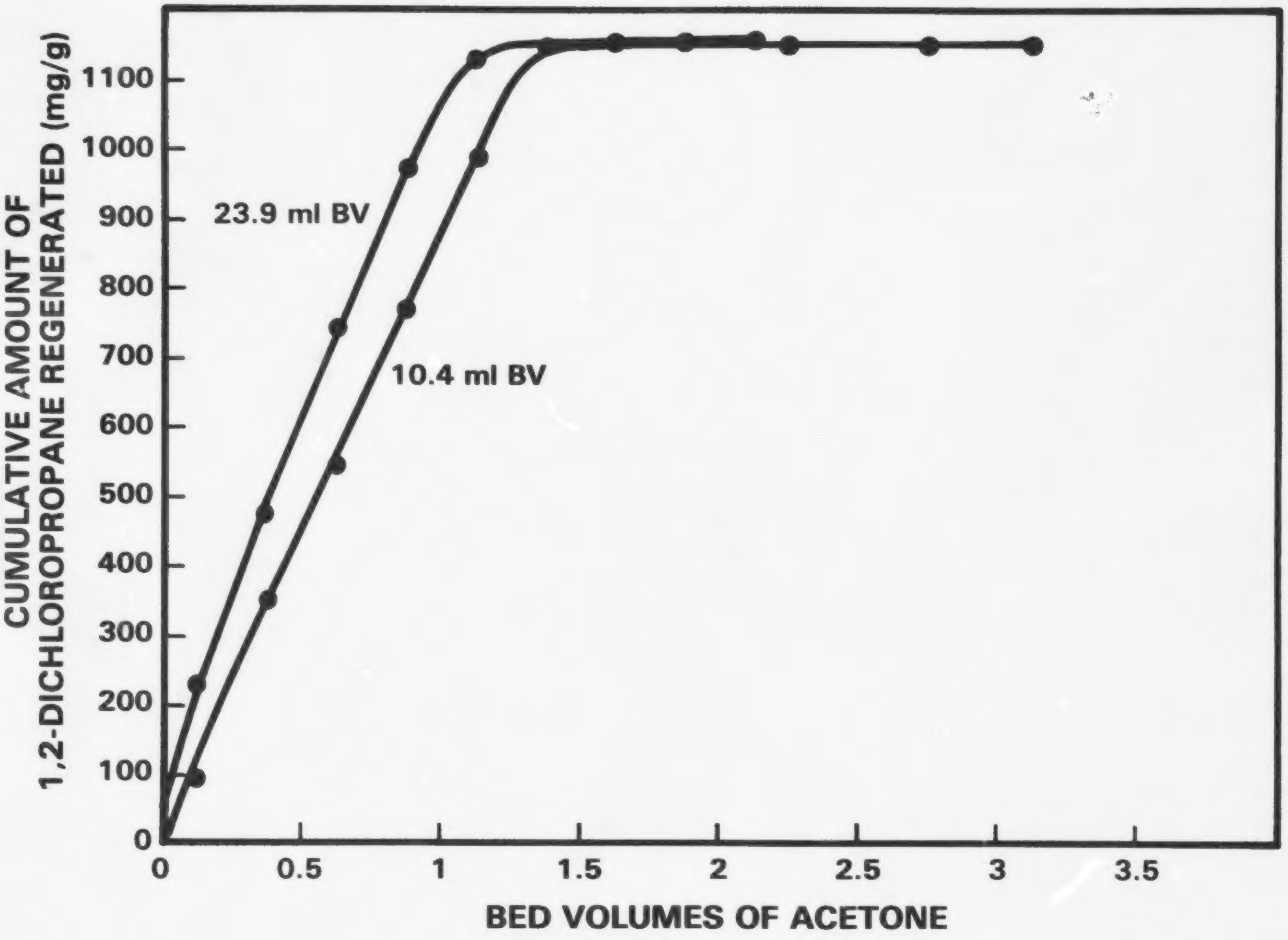


FIGURE 30. COLUMN REGENERATION OF 1,2-DICHLOROPROPANE LOADED AMBERLITE XAD-4

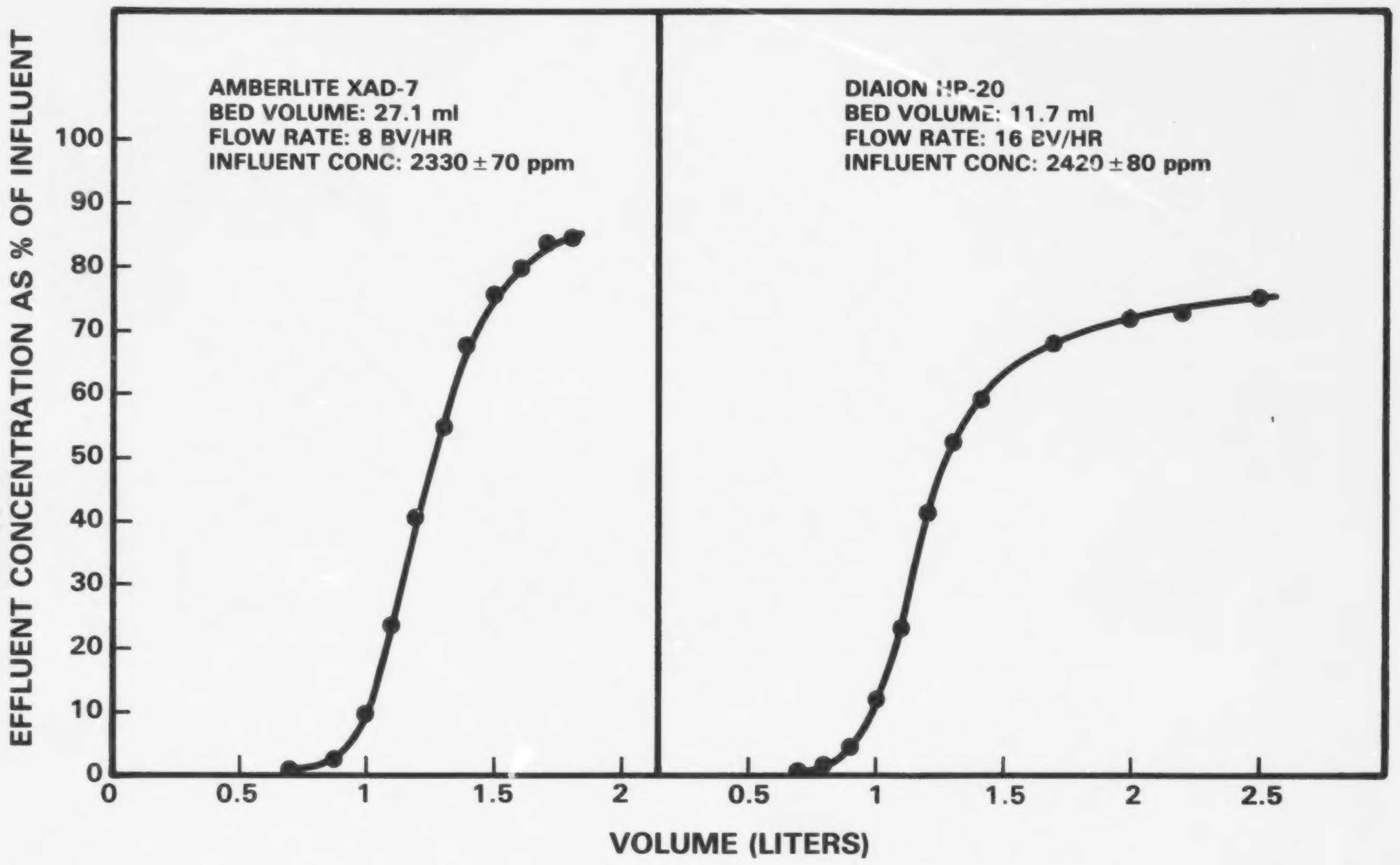


FIGURE 31. COLUMN ADSORPTION OF 1,2-DICHLOROPROPANE BY SELECTED ADSORBENTS

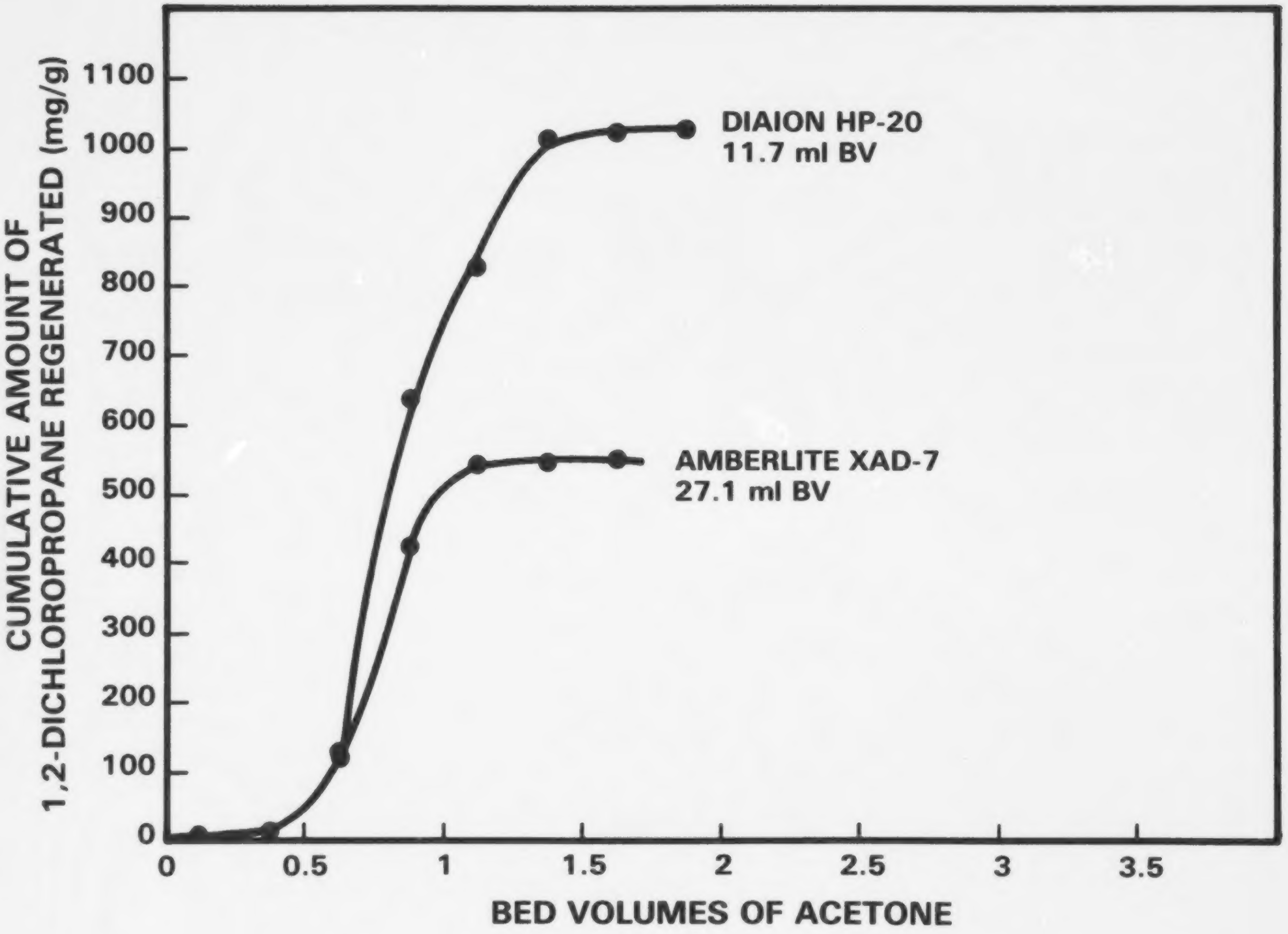


FIGURE 32. COLUMN REGENERATION OF 1,2-DICHLOROPROPANE LOADED ADSORBENTS

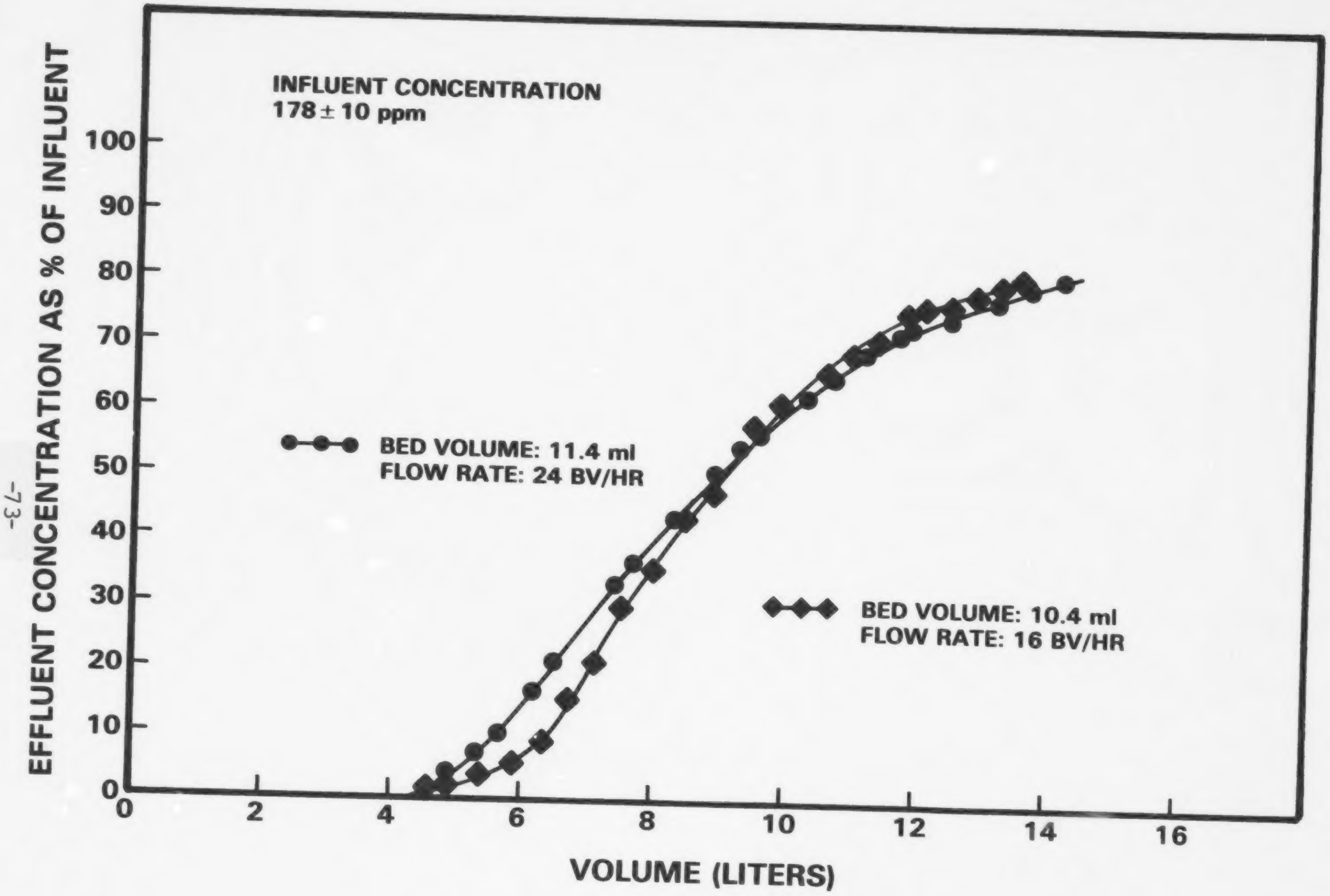


FIGURE 33. COLUMN ADSORPTION OF 2,4-DINITROTOLUENE BY AMBERLITE XAD-4

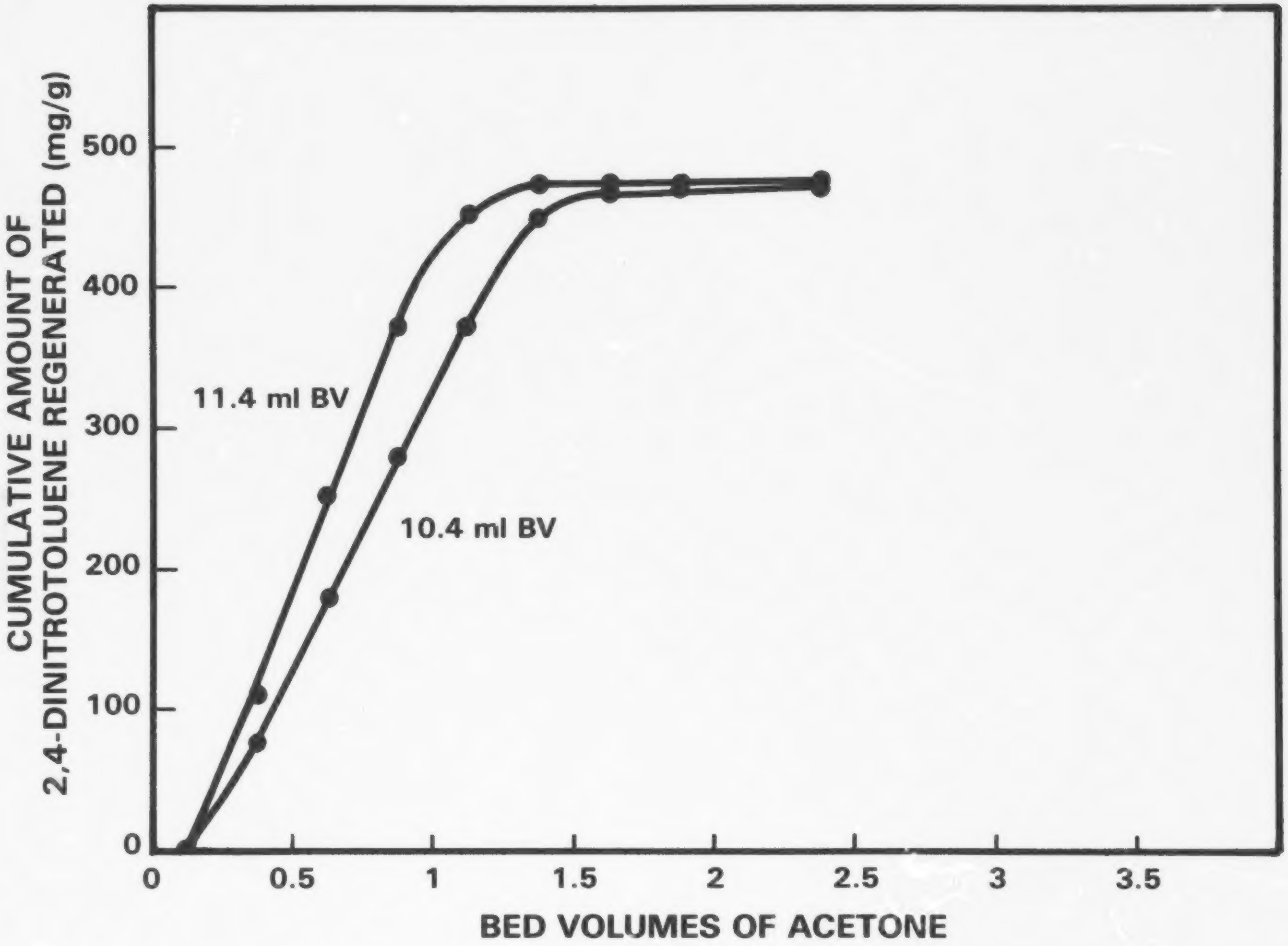


FIGURE 34. COLUMN REGENERATION OF 2,4-DINITROTOLUENE LOADED AMBERLITE XAD-4

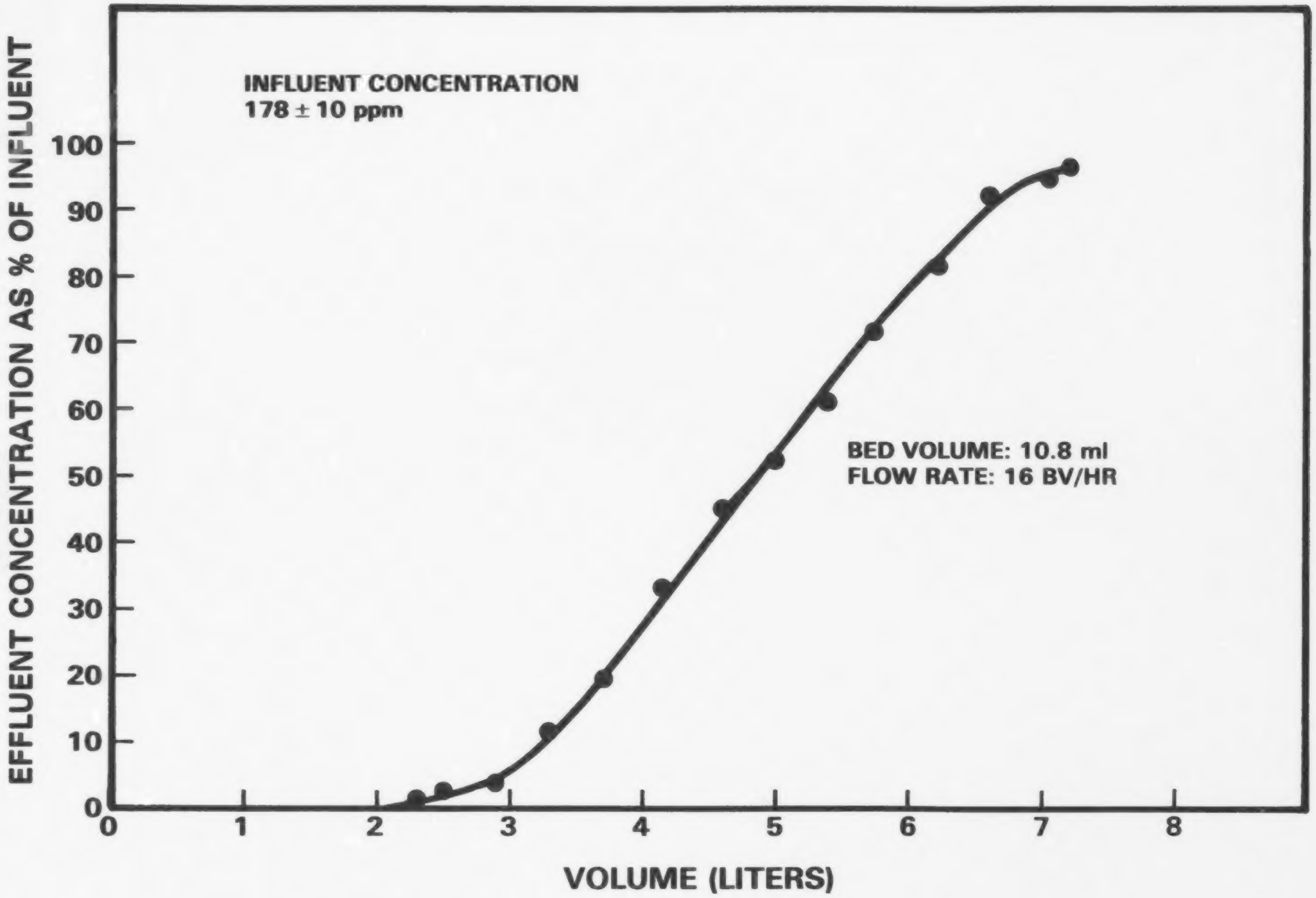


FIGURE 35. COLUMN ADSORPTION OF 2,4-DINITROTOLUENE BY AMBERSORB XE-340

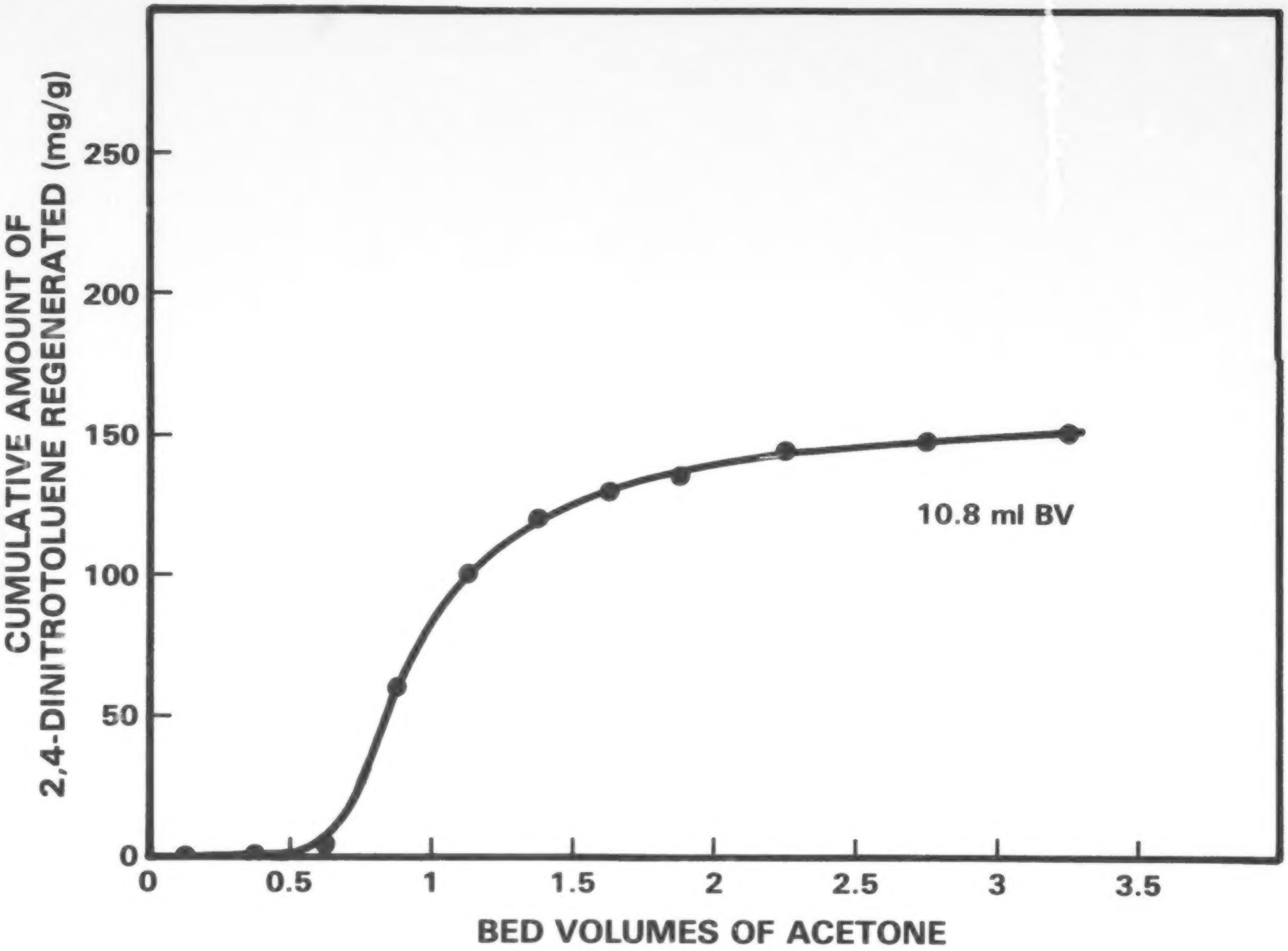


FIGURE 36. COLUMN REGENERATION OF 2,4-DINITROTOLUENE LOADED AMBERSORB XE-340

Synthetic, Nitroaromatic Stream

The average concentrations of organic pollutants in the multicomponent stream used for column studies were: 200 ppm toluene, 679 ppm nitrobenzene, 506 ppm 2-nitrophenol, and 52 ppm 2,4-dinitrotoluene. Although the synthetic waste stream system (vide supra) provided a fairly constant total waste stream concentration to within 5% of the average, a 12% fluctuation was observed in toluene concentration, perhaps due to its greater volatility as compared to the nitroaromatics. Column loading was continued until NB and NPL leakage approached (or exceeded) 100% breakthrough. Generally, NPL breakthrough exceeded 100% before column loading was terminated. This was due to displacement of adsorbed NPL by other waste stream components which were more strongly adsorbed by the resins. The linear equilibrium constants are a measure of this preferential adsorption (see Table 25).

In all studies the order of leakage was NPL, NB, then T. DNT, which contributed only 4% to the total influent concentration, was never detected in the column effluent. Since the lower limit of GC sensitivity to DNT in this waste stream was 5 to 10 ppm, DNT breakthrough of 10 to 20% could go undetected. This was not a problem in the single component DNT study where the lower limit of GC sensitivity was 1 to 2 ppm. Acetone regeneration adequately displaced NB, NPL, and DNT from the loaded columns. However, large discrepancies between loading and regeneration data for toluene indicate that the chosen regeneration conditions did not effectively remove adsorbed toluene (vide infra).

Two 10.6 mL BV columns of Amberlite XAD-4 were loaded with the nitroaromatic stream. The breakthrough curves for the column loaded at 8 BV/hr are displayed in Figure 37 while those for the column loaded at 16 BV/hr appear in Figure 38. Cumulative saturation capacities are 1025 mg/g (8 BV/hr column) and 1079 mg/g (16 BV/hr column). Within the ±5% error limits, doubling the flow rate did not significantly alter saturation capacity. Capacity to 10% breakthrough was also not significantly altered. For example, for the 8 BV/hr column, NB capacity is 376 mg/g and NPL capacity is 268 mg/g. At the faster flow rate these capacities are 355 mg/g and and 252 mg/g respectively. Results of acetone regeneration of these columns are shown in Figures 39 and 40. Regeneration appeared to be complete in 2 BV. However, toluene was never fully regenerated. Cumulative amounts of organic regenerated are 976 mg/g (8 BV/hr column) and 994 mg/g (16 BV/hr) for an average regeneration efficiency of ca. 93%.

Similarly, two equal length columns of Diaion HP-20 were loaded at two different flow rates: 12.5 mL BV loaded at 8 BV/hr and 12.2 mL BV loaded at 16 BV/hr. The breakthrough characteristics of these columns are shown in Figures 41 and 42. Pressure drop across these columns was a constant problem. Pumping rates had to be frequently increased in order to maintain the desired flow through the beds. Cumulative column saturation capacities are 849 mg/g (8 BV/hr column) and 896 mg/g (16 BV/hr column). Again, these flow rates produced nearly identical capacities to 10% breakthrough: 328 ± 6 mg/g for NB and 224 ± 2 mg/g for NPL. Acetone regeneration results are displayed in Figures 43 and 44. Excluding toluene which was not fully

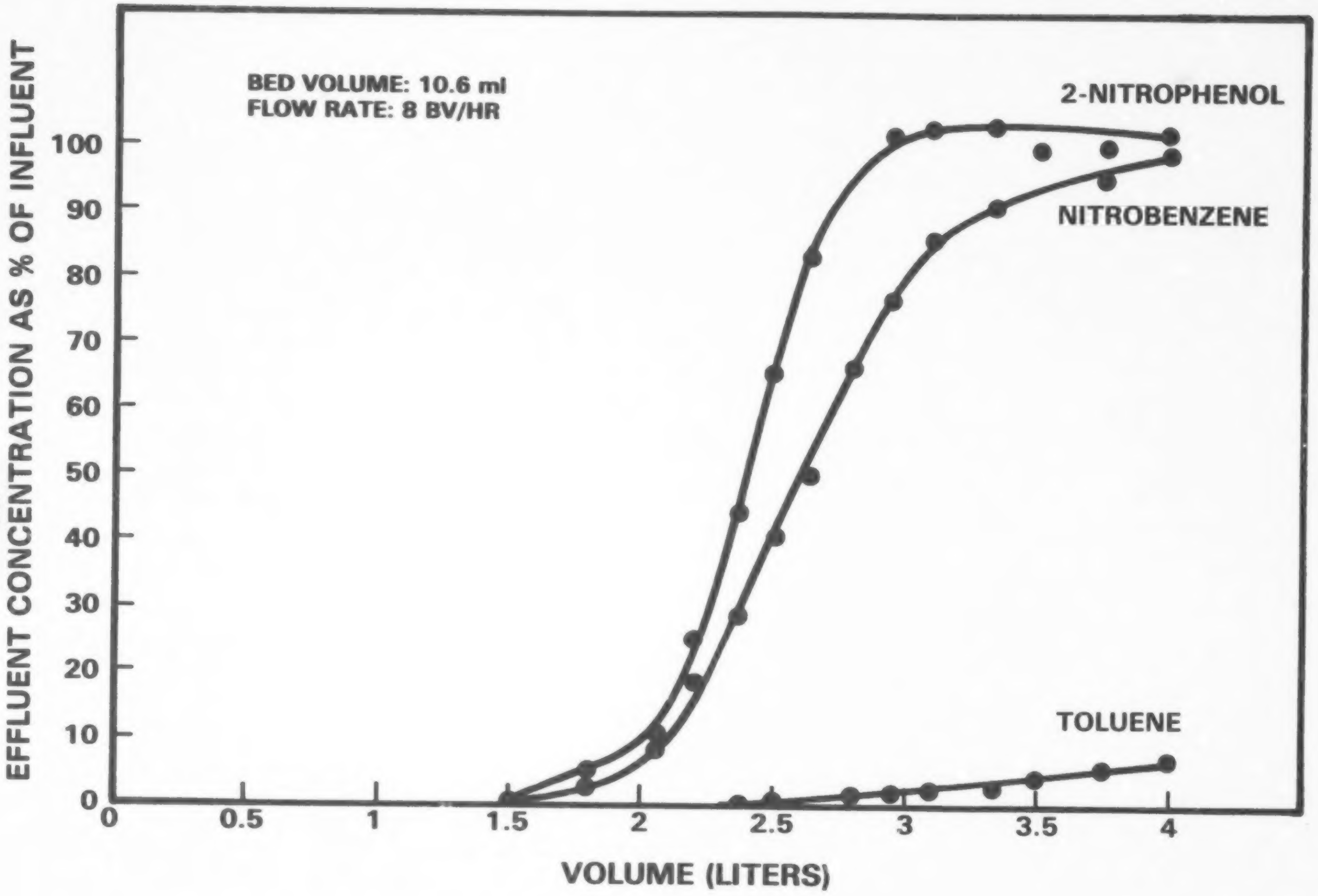


FIGURE 37. COLUMN ADSORPTION OF NITROAROMATICS BY AMBERLITE XAD-4

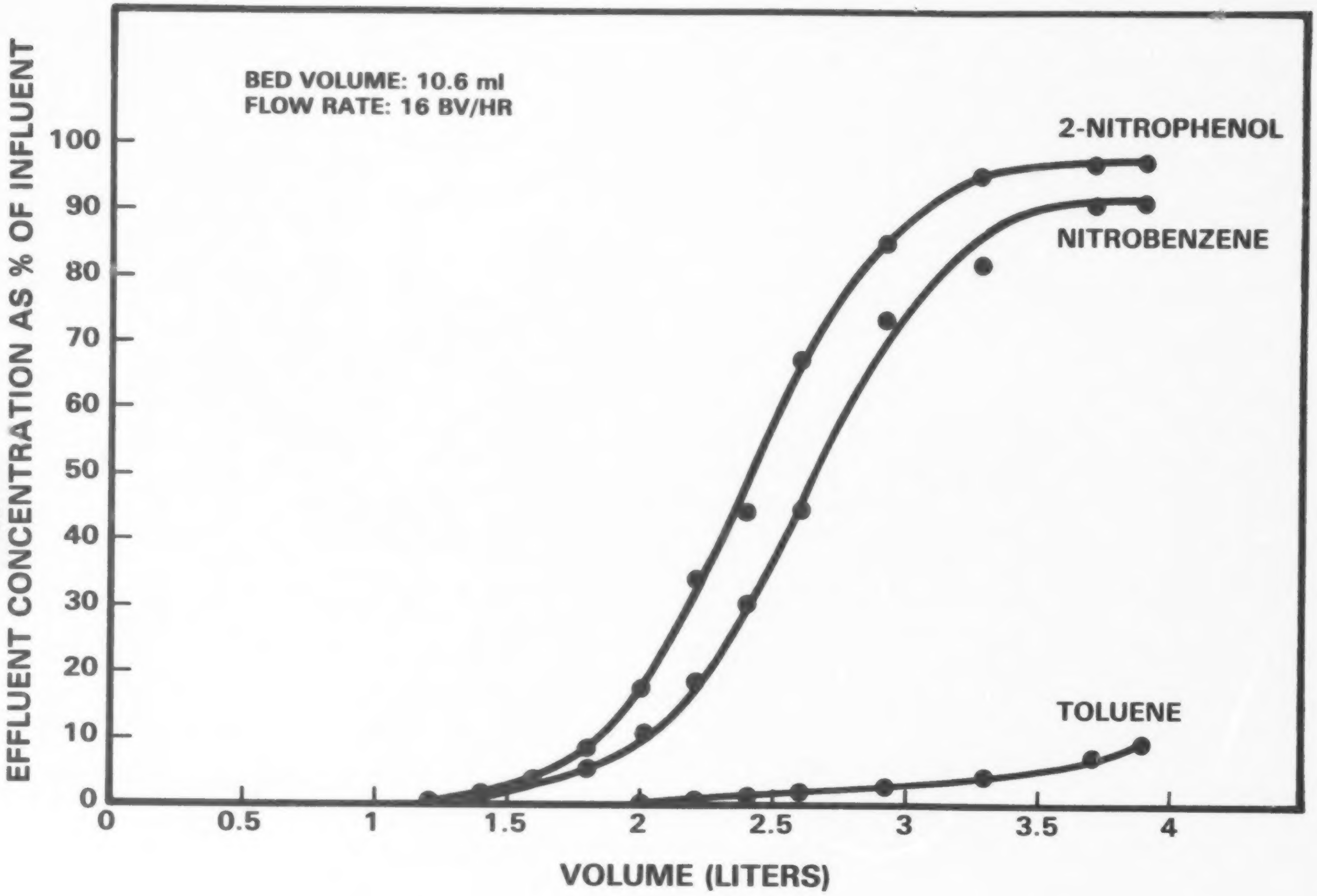


FIGURE 38. COLUMN ADSORPTION OF NITROAROMATICS BY AMBERLITE XAD-4

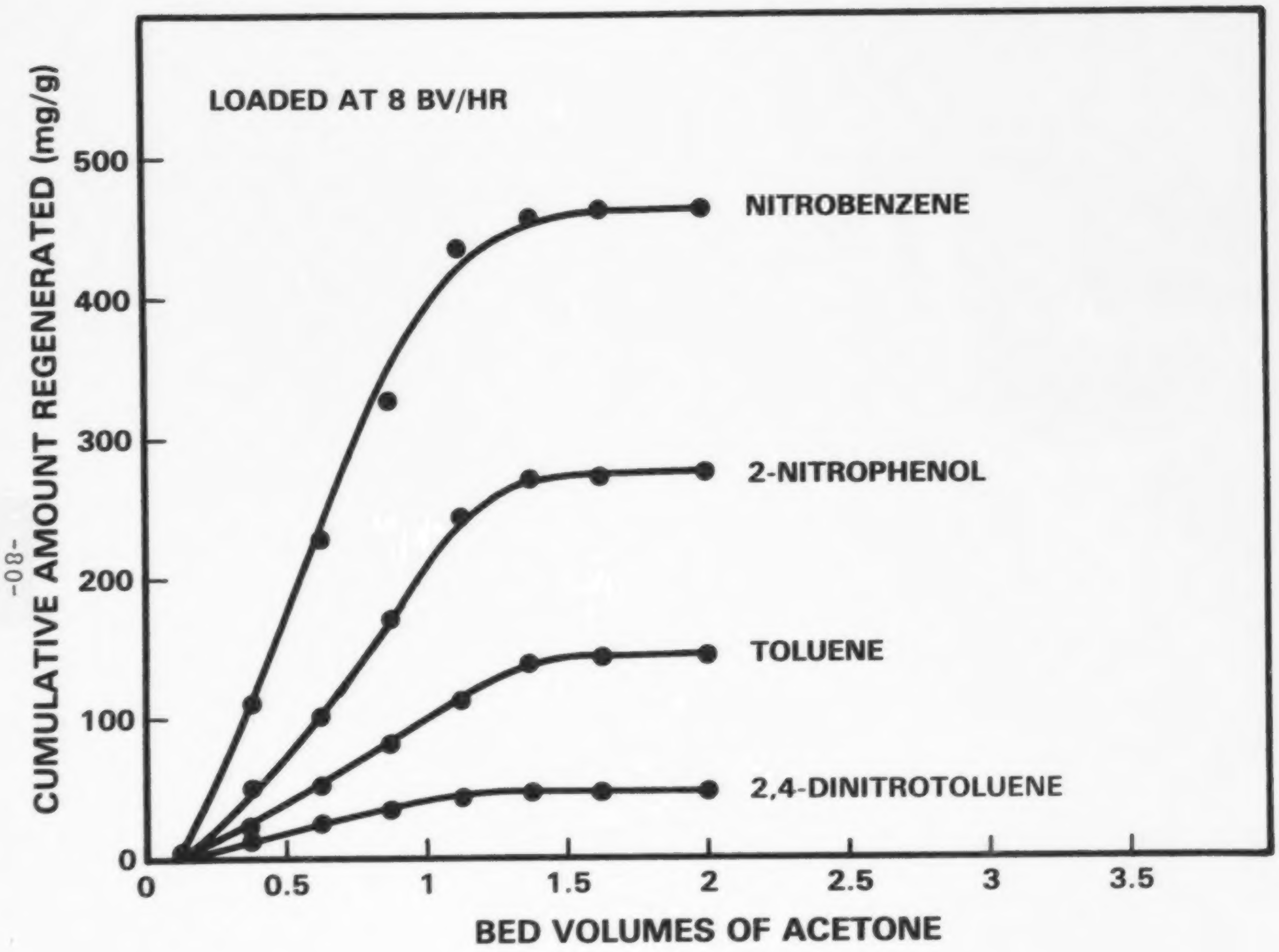


FIGURE 39. COLUMN REGENERATION OF NITROAROMATICS LOADED AMBERLITE XAD-4

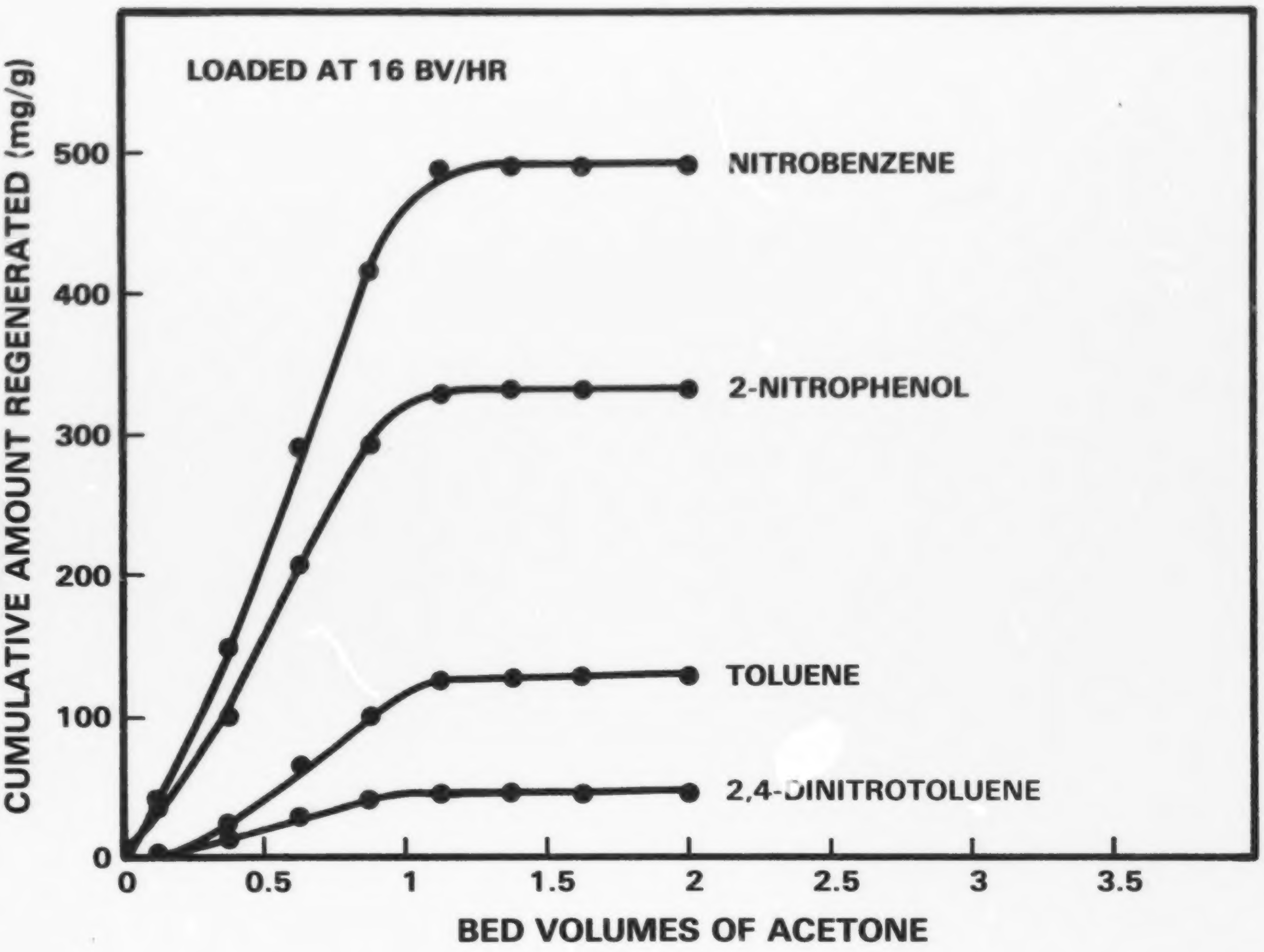


FIGURE 40. COLUMN REGENERATION OF NITROAROMATICS LOADED AMBERLITE XAD-4

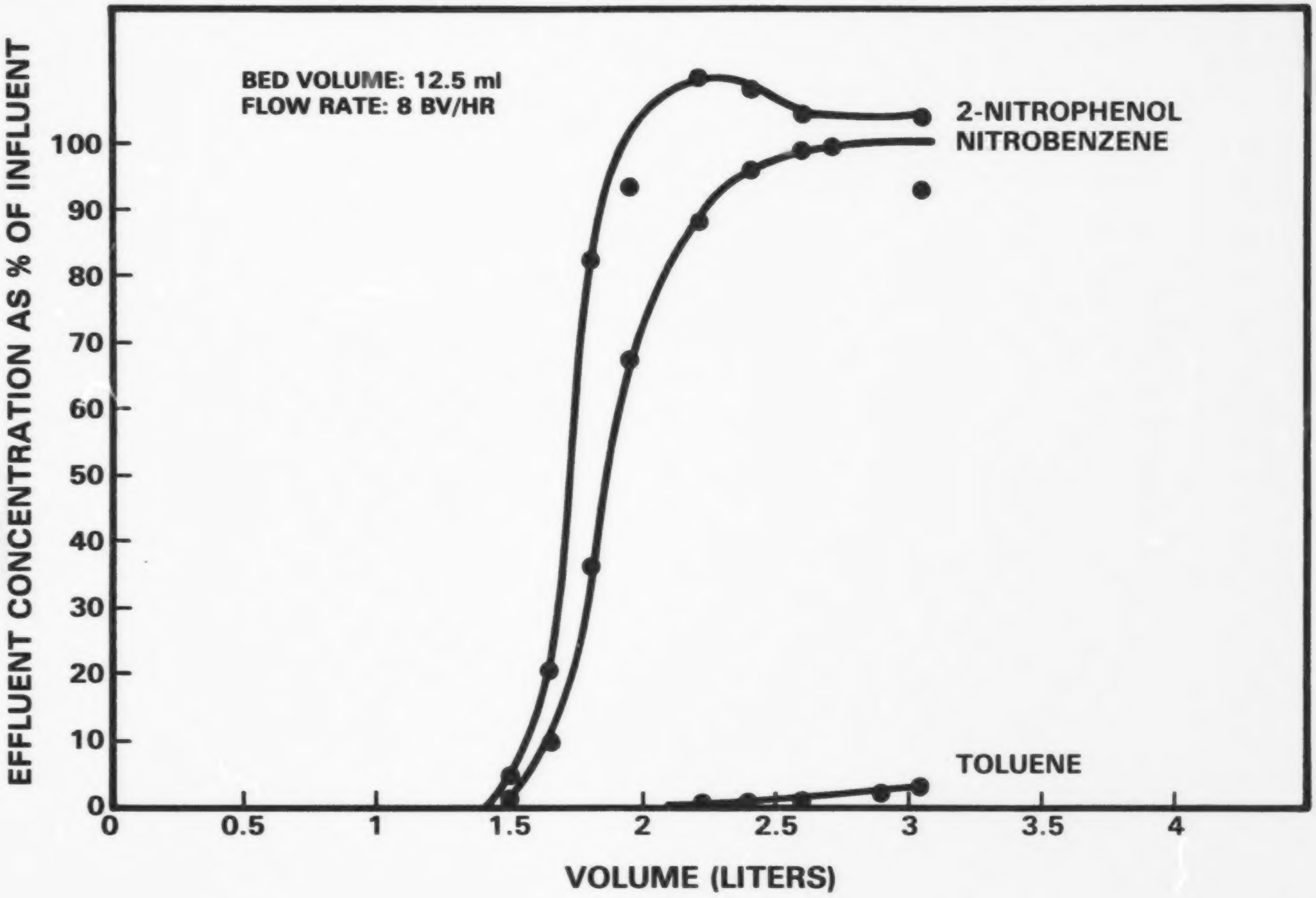


FIGURE 41. COLUMN ADSORPTION OF NITROAROMATICS BY DIAION HP-20

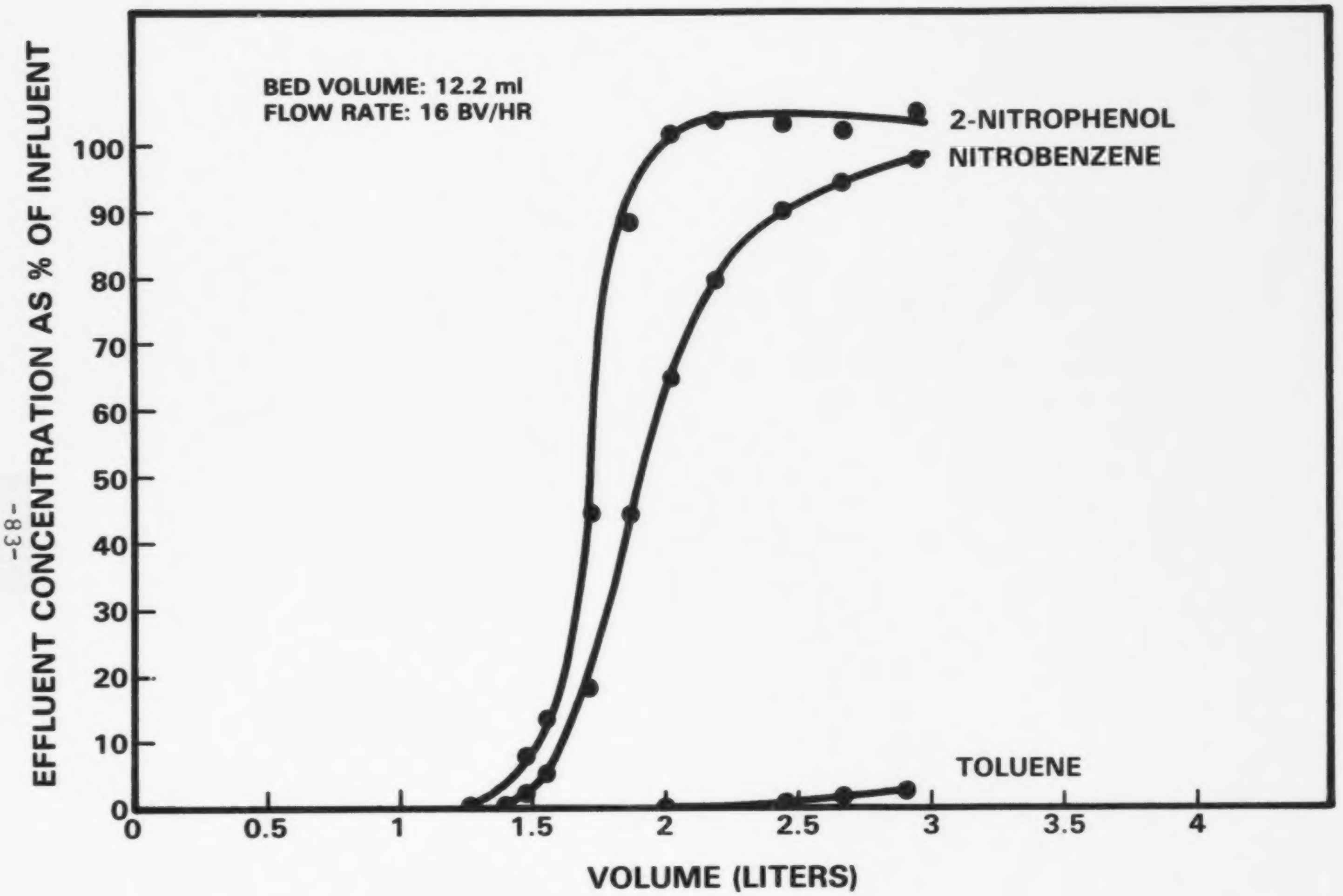


FIGURE 42. COLUMN ADSORPTION OF NITROAROMATICS BY DIAION HP-20

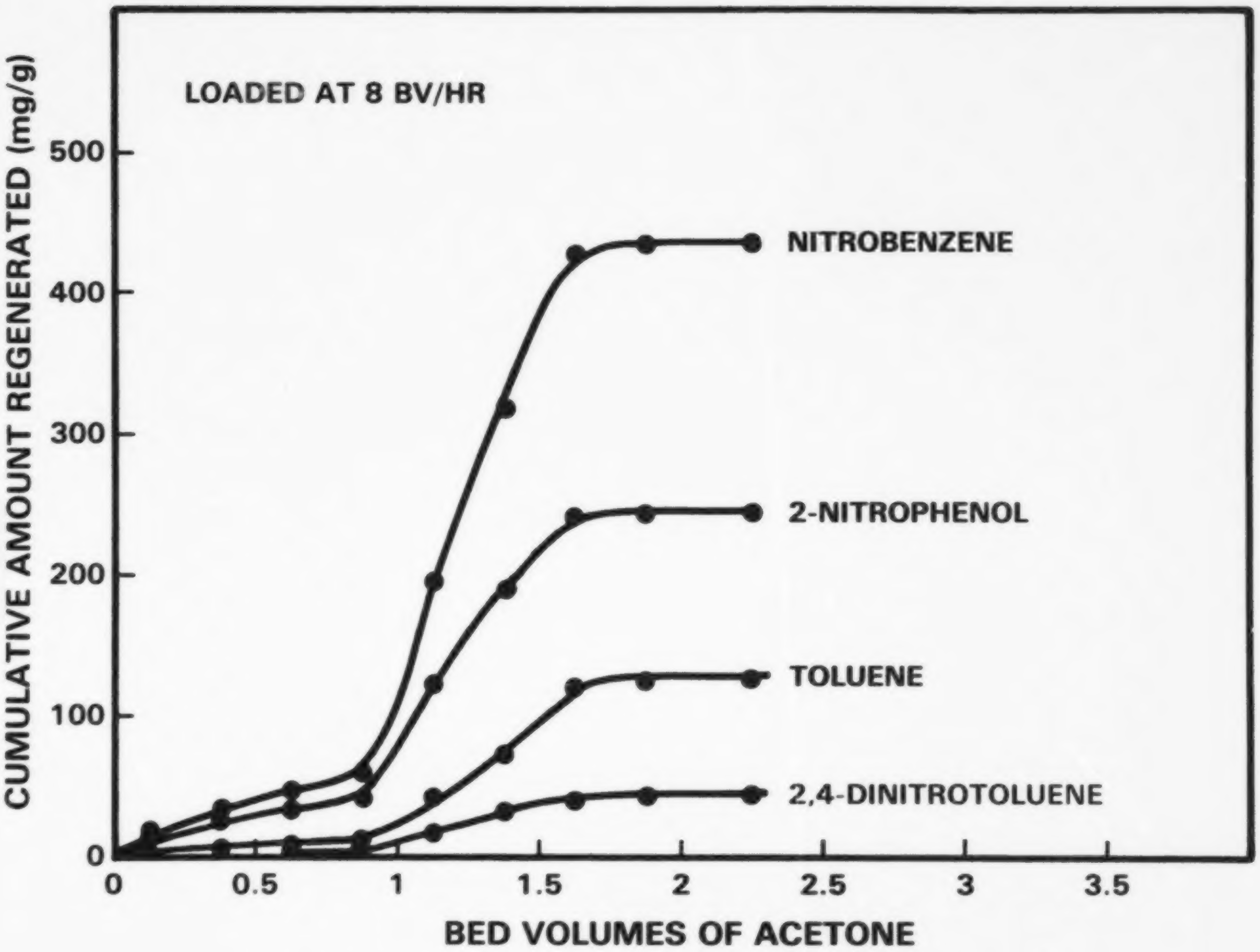


FIGURE 43. COLUMN REGENERATION OF NITROAROMATICS LOADED DIAION HP-20

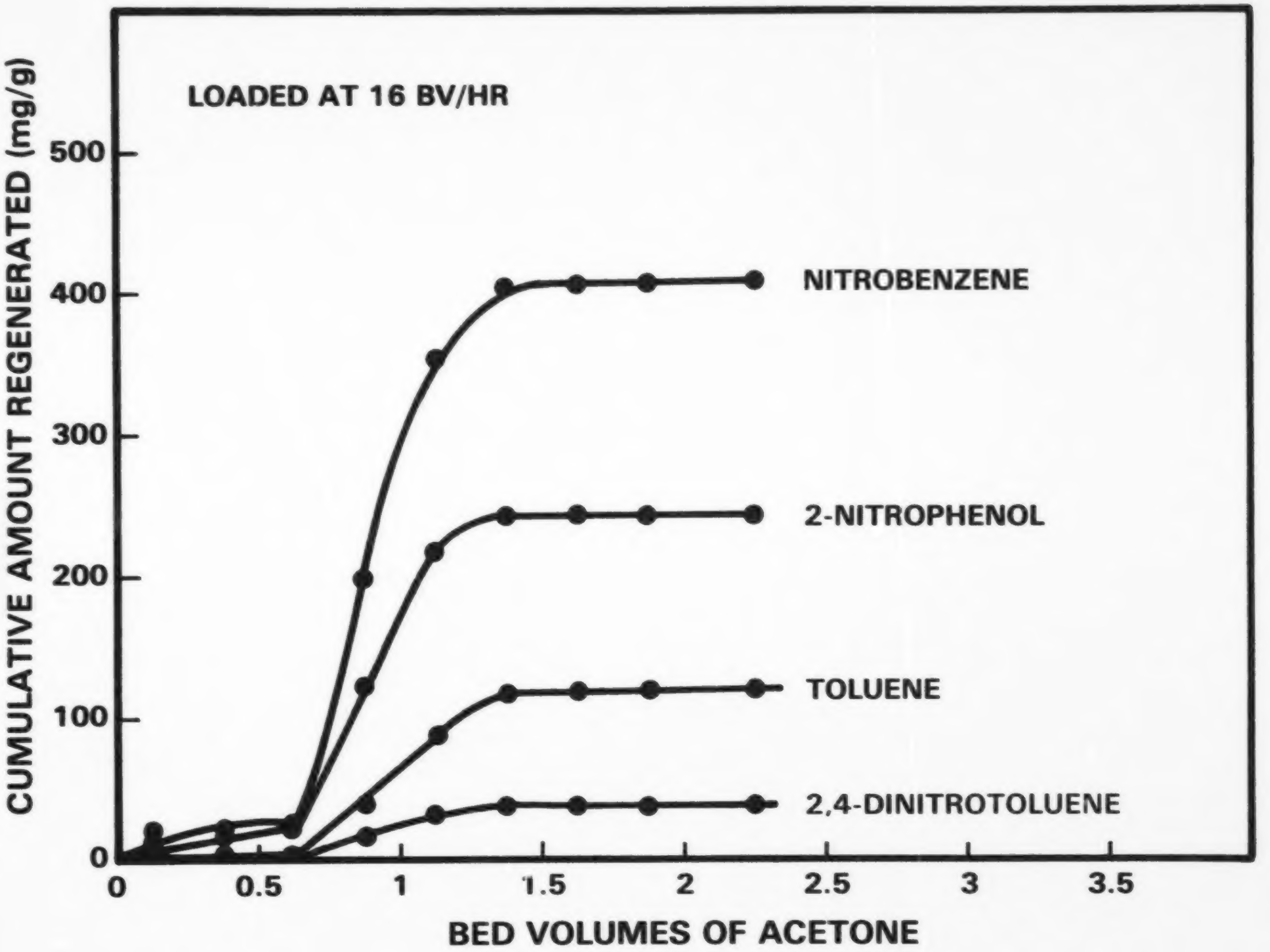


FIGURE 44. COLUMN REGENERATION OF NITROAROMATICS LOADED DIAION HP-20

regenerated, regeneration was complete in 2 BV. Regenerated column capacities are 844 mg/g (8 BV/hr column) and 801 mg/g (16 BV/hr column) or an average efficiency of ca. 94%.

To provide additional data for correlating batch/rate data and column performance for carbonaceous adsorbents, an 11.0 mL BV column of Ambersorb XE-340 was loaded with the nitro-aromatic stream at 8 BV/hr as shown in Figure 45. Initial breakthrough of NPL, NB, and T occurred almost concurrently unlike breakthrough behavior observed with the polymeric resins. Saturation capacity is 274 mg/g. Regeneration required 4 BV of acetone (see Figure 46) and resulted in a regeneration capacity of 249 mg/g or 91% efficiency.

A report from an EPA funded study of priority pollutant treatability using three technologies (carbon adsorption, resin adsorption, and steam stripping) is related to this study. A complex industrial waste stream was used and treatability was assessed by monitoring five priority pollutants: chlorobenzene, dichlorobenzene, nitrobenzene, dinitrotoluene, and phenol. The results indicate that both carbon and resin adsorption are feasible methods of treating the waste stream in question. The authors observed that resin (XAD-4) capacity improved with several loading/regeneration cycles[16]. This indicates that the resin was not fully conditioned prior to use in the isotherm tests and column experiments. Thus, reported capacities were underestimated and treatment costs were probably overestimated. This illustrates the importance of carefully pre-conditioning synthetic adsorbents prior to use to remove residual salts and organics from their pores.

SUMMARY OF ADSORPTION DATA

The saturation capacities as measured by isotherm, batch and column studies of various adsorbents in the single component waste streams are recorded in Table 27. In general, the batch test performs better than the isotherm test in predicting column saturation capacities for these compounds. It provides a more accurate evaluation of column saturation than the isotherm test and requires only a single analysis after adsorbent exposure to the influent waste stream. 2-Nitrophenol data are fairly scattered and good comparisons are therefore difficult to make. This is because test method development occurred primarily during the 2-nitrophenol study. This study was not repeated after the incorporation of improvements in experimental procedures. Carbon adsorption data are not included here. Because the batch/rate test measures regenerated capacity, it is not generally useful in assessing carbon capacity. Experimental procedures for measuring the capacity of activated carbon have been reported elsewhere[9].

The saturation capacities as measured by batch and column studies of various adsorbents in the synthetic, nitroaromatic stream are listed in Table 28. Based on results from single component stream testing, the isotherm test was eliminated in the 4-component stream study. Since column saturation was achieved only with nitrobenzene and 2-nitrophenol, batch and column data can be compared for these two compounds only. Despite fluctuations in waste stream concentrations (see Table 28), the single analysis batch test adequately predicts column saturation capacities with the multicomponent stream.

Column loading is typically stopped at some predetermined level of breakthrough such as 10% leakage rather than at saturation. To provide a more realistic picture of usable column capacity, both bed volumes of waste stream treated and column capacities for each component to 1% and 10% leakage have been obtained from column loading experiments. These data are recorded in Table 29 for three single component streams and in Table 30 for the synthetic, nitroaromatic stream. To test flow rate effects, column loading of Amberlite XAD-4 was done at two different flow rates with all four streams. Diaion HP-20 was also used in flow rate studies with the multicomponent stream. In the single component stream studies, increasing the flow from 8 to 16 BV/hr (1 to 2 gpm/ft^3) or from 16 to 24 BV/hr (2 to 3 gpm/ft^3) resulted in approximately 15% capacity loss to 10% leakage. In the multicomponent stream studies, a similar increase in flow only decreased the capacity about 5%. In real applications, these fairly rapid flows (16 BV/hr) would provide optimum use of column capacity. Since flow rates depend on the particular adsorbent, waste stream components and concentrations, system design, and the tolerable level of breakthrough components, they must be determined for each application. Past applications of polymeric adsorbents have typically used flows of 2 to 12 BV/hr (0.25 to 1.5 gpm/ft^3) [5,16,17].

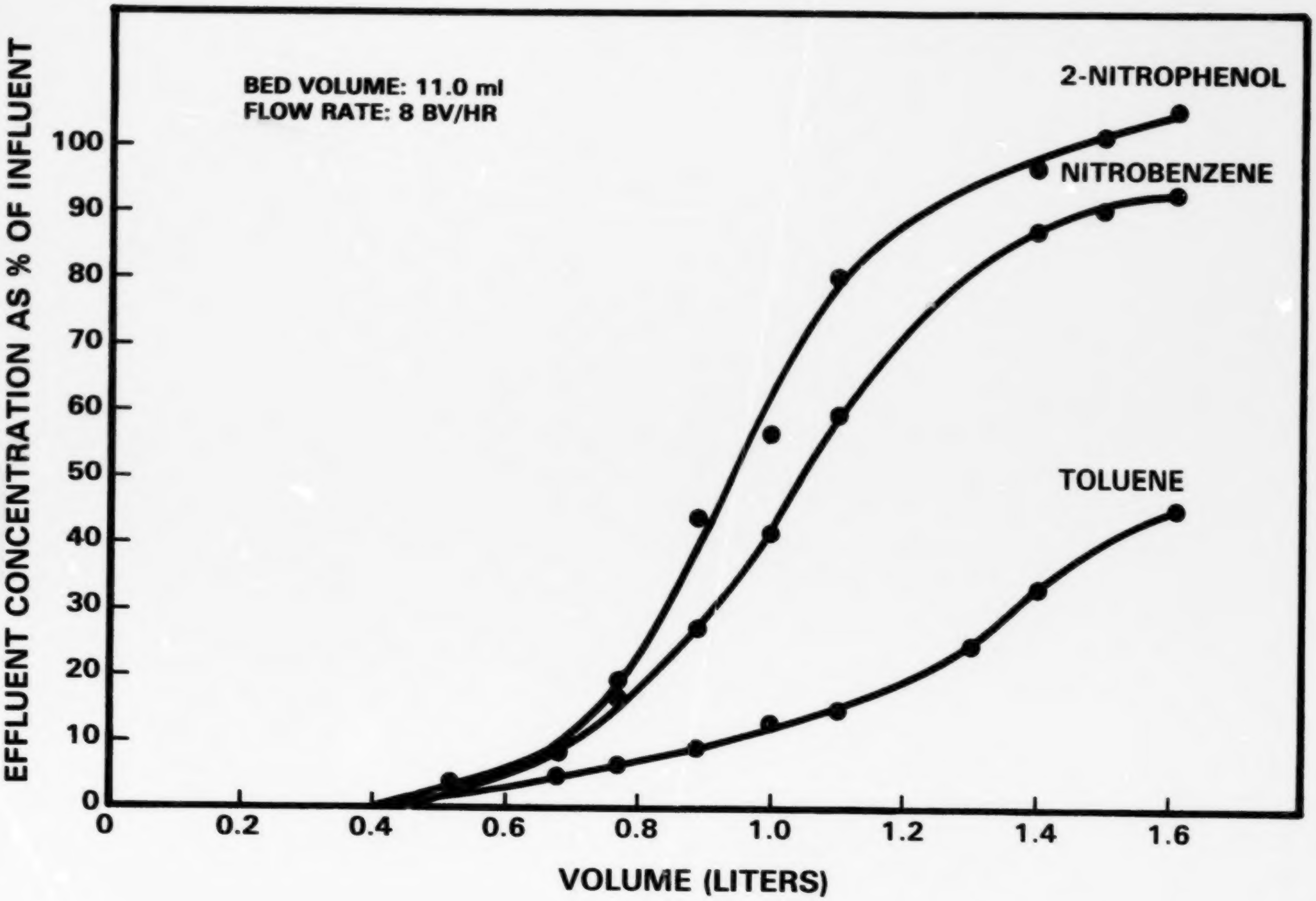


FIGURE 45. COLUMN ADSORPTION OF NITROAROMATICS BY AMBERSORB XE-340

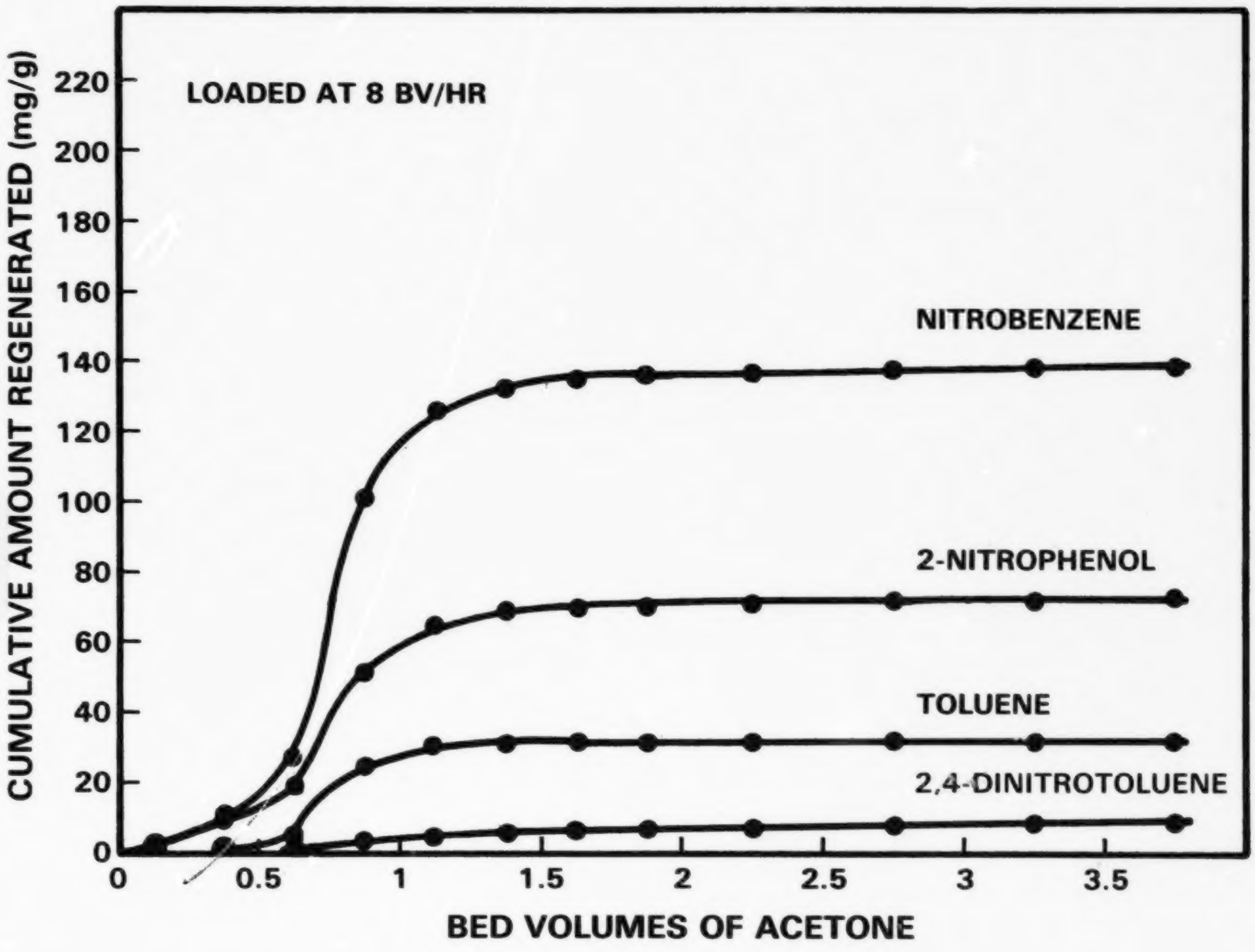


FIGURE 46. COLUMN REGENERATION OF NITROAROMATICS LOADED AMBERSORB XE-340

TABLE 27

SUMMARY OF SATURATION CAPACITIES MEASURED BY ISOTHERMS, BATCH TESTS, AND COLUMN EXPERIMENTS IN SINGLE COMPONENT WASTE STREAMS (mg/g)

Adsorbate[a]	Adsorbent	Isotherm[b]	Batch	BV(mL)	Flow (BV/hr)	Column Loading	Column Regeneration
2-Nitrophenol(pH 5)	XAD-4	1120, 1260	518	24.0	8	684	847
				12.0	16	922	739
2-Nitrophenol(pH 8)	XAD-4	228, 261	348	24.0	8	299	231
				12.0	16	282	272
2-Nitrophenol(pH 5)	XAD-8	592, 704	245	24.0	8	247	332
2-Nitrophenol(pH 8)	XAD-8	159, 227	145	24.0	8	124	82
Nitrobenzene	XAD-4	859	1310	23.1	8	1330	1250
				11.0	16	1260	1080
Nitrobenzene	XAD-8	456	580	11.6	16	569	530
Nitrobenzene	HP-20	670	1160	24.3	8	1150	1060
1,2-Dichloropropane	XAD-4	747	1070	23.9	8	1310	1150
				10.4	16	1240	1160
1,2-Dichloropropane	XAD-7	409	564	27.1	8	523	544
1,2-Dichloropropane	HP-20	778	1060	11.7	16	1200	1030
2,4-Dinitrotoluene	XAD-4	397	450	10.4	16	434	470
				11.4	24	432	474
2,4-Dinitrotoluene	XE-340	118	138	10.8	16	148	151

[a] Aqueous 2-nitrophenol conc. (mg/L): isotherm = 750, 1000; batch = 750 (pH 5), 820 (pH 8); column = 1070 (XAD-4), 675 (XAD-8, pH 5), 790 (XAD-8, pH 8)
Aqueous nitrobenzene conc. (mg/L): isotherm = 1900; batch = 1900; column = 1800
Aqueous 1,2-dichloropropane conc. (mg/L): isotherm = 2500; batch = 2450; column = 2350
Aqueous 2,4-dinitrotoluene conc. (mg/L): isotherm = 180; batch = 180; column = 180

[b] Capacities calculated from Freundlich parameters assuming linear isotherms.

TABLE 28

SUMMARY OF SATURATION CAPACITIES MEASURED BY BATCH TESTS AND COLUMN EXPERIMENTS IN THE SYNTHETIC, NITROAROMATIC STREAM (mg/g)

Adsorbent	Adsorbate[a]	Batch	BV (mL)	Flow (BV/hr)	Column Loading[b]	Column Regeneration[b]
XAD-4	Toluene	183	10.6	8	181	144
	Nitrobenzene	575			479	512
	2-Nitrophenol	292			308	273
	2,4-Dinitrotoluene	141			57	47
XAD-4	Toluene	183	10.6	16	206	127
	Nitrobenzene	575			486	490
	2-Nitrophenol	292			335	332
	2,4-Dinitrotoluene	141			52	45
XE-340	Toluene	37	11.0	8	52	31
	Nitrobenzene	131			125	138
	2-Nitrophenol	72			83	72
	2,4-Dinitrotoluene	46			14	8
HP-20	Toluene	178	12.5	8	170	126
	Nitrobenzene	525			392	433
	2-Nitrophenol	276			241	243
	2,4-Dinitrotoluene	127			46	42
HP-20	Toluene	178	12.2	16	180	118
	Nitrobenzene	525			395	406
	2-Nitrophenol	276			248	241
	2,4-Dinitrotoluene	127			43	36

CONTINUED

TABLE 28 (CONTINUED)

SUMMARY OF SATURATION CAPACITIES MEASURED BY BATCH TESTS AND COLUMN EXPERIMENTS IN THE SYNTHETIC, NITROAROMATIC STREAM (mg/g)

Notes

a Ave. waste stream concentration (mg/L) varied from test to test as indicated below:

Test	Toluene	Nitrobenzene	2-Nitrophenol	2,4-Dinitrotoluene
Batch (all)	239	708	506	48
XAD-4 (8)	175	686	507	55
XAD-4 (16)	205	683	522	51
XE-340 (8)	220	678	515	51
HP-20 (8)	190	685	495	51
HP-20 (16)	210	665	490	50

b Column saturation was attained with nitrobenzene and 2-nitrophenol only. Column capacities for toluene and 2,4-dinitrotoluene are not saturation capacities.

TABLE 29

SUMMARY OF COLUMN CAPACITY DATA FOR THE SINGLE COMPONENT WASTE STREAMS

Adsorbent	Flow (BV/hr)	Adsorbate[a]-Ave. Conc. (mg/L)	BV to 1% Leakage	Capacity at 1% Leakage (mg/g)	BV to 10% Leakage	Capacity at 10% Leakage (mg/g)
XAD-4	8	NB-1805	173	918	199	1056
XAD-4	16	NB-1805	143	743	179	930
XAD-8	16	NB-1805	34	239	49	344
HP-20	8	NB-1805	119	847	133	947
XAD-4	8	PDC-2350	105	647	143	881
XAD-4	16	PDC-2350	77	490	115	731
XAD-7	8	PDC-2330	28	300	37	394
HP-20	16	PDC-2420	64	581	85	771
XAD-4	16	DNT-178	438	211	617	297
XAD-4	24	DNT-178	390	201	490	253
XE-340	16	DNT-178	210	68	304	99

[a] NB - nitrobenzene
PDC - 1,2-dichloropropane
DNT - 2,4-dinitrotoluene

TABLE 30

SUMMARY OF COLUMN CAPACITY DATA FOR THE SYNTHETIC, NITROAROMATIC WASTE STREAM

Adsorbent	Flow (BV/hr)	Adsorbate[a,b]-Ave. Conc.(mg/L)	BV to 1% Leakage	Capacity at 1% Leakage (mg/g)	BV to 10% Leakage	Capacity at 10% Leakage (mg/g)
XAD-4	8	T-175	236	114	>>377[c]	>>183[c]
		NB-686	156	296	198	376
		NPL-507	142	199	172	268
XAD-4	16	T-205	212	121	>368[c]	>210[c]
		NB-683	132	252	186	355
		NPL-522	123	179	172	251
XE-340	8	T-220	41	17	82	34
		NB-678	38	49	64	81
		NPL-515	36	35	62	60
HP-20	8	T-190	200	141	>>244[c]	>>170[c]
		NB-685	120	303	132	333
		NPL-495	112	204	124	226
HP-20	16	T-210	205	156	>>238[c]	>>180[c]
		NB-665	117	282	133	322
		NPL-490	111	197	125	222

[a] Waste stream components: Toluene(T), nitrobenzene(NB), 2-nitrophenol(NPL), and 2,4-dinitrotoluene(DNT)

[b] Since DNT (influent conc. 50 mg/L) was never detected in the column effluent, it is not included in this table.

[c] Column loading of XAD-4 and HP-20 columns was terminated before toluene leakage reached 10%.

SECTION 7

PREDICTIONS OF COLUMN PERFORMANCE USING BATCH/RATE DATA

PREDICTIONS BASED ON THE PERFORMANCE MODEL

Many models for predicting the performance of ion exchange and carbon adsorption columns from equilibrium and kinetic data have appeared in the chemical literature over the past 30 to 40 years [18-26]. More recently, models for predicting column performance of synthetic adsorbents also have been published [27,28]. These models are generally very complex and require the determination of many experimental parameters as well as the execution of complicated (often computer-based) calculations. A simplified model for predicting column performance of ion exchange resins has been developed at Rohm and Haas. The theoretical basis for this model is presented in Appendix C. This model can predict performance under a wide range of operating conditions from a limited amount of experimental data, i.e., either a single column loading/regeneration experiment or simple equilibrium and kinetic batch experiments. This model, used as developed for ion exchange columns, also works satisfactorily for predicting performance of synthetic adsorbents from data obtained using the new batch/rate test method. Although refinement of this model may be desired to improve predictions, in its present form it is extremely attractive for several reasons: 1) only a very limited amount of readily obtained data is required, 2) data manipulation is simple, 3) the mass transfer coefficient is determined graphically from simple capacity measurements (Figure C-1), 4) column performance can be obtained graphically (Figure C-2) or from various tables developed for fixed-bed heat transfer, the J function [18,29,30].

The equations used in the following sections are developed and defined in Appendix C. The definitions and units for symbols used in these equations appear in Appendix D.

APPLICATIONS OF THE PERFORMANCE MODEL

An example calculation using the performance model is presented here for adsorption of 1,2-dichloropropane on Amberlite XAD-4 columns. In order to predict column performance and develop a concentration history graph or breakthrough curve, the linear equilibrium constant, K in cc/g, must be calculated from batch data and the mass transfer coefficient or rate constant, k in min^{-1}, must be calculated from rate data. In addition to these two experimentally determined parameters (K and k) several physical/geometrical parameters of the resin are required, as well as a set of chosen column operating conditions. These parameters can be measured by conventional methods, obtained from the resin manufacturer, or simply estimated.

Calculation of the Linear Equilibrium Constant

Using experimental batch data for adsorption of PDC by Amberlite XAD-4 (Table 16), the linear equilibrium constant is calculated as follows:

$$K_B = \frac{Q_{sat}}{C_s} \times 1000 = \frac{1075}{2450} \times 1000 = 440 \text{ cc/g}$$

To adjust for non-linearity of the equilibrium behavior at high solution concentrations, an empirical correction factor has been applied to K_B as follows:

$$K_{B'} = 1.1\ K_B = 480 \text{ cc/g}$$

Calculation of the Mass Transfer Coefficient

The various parameters needed to calculate the mass transfer coefficient are listed in Table 31. The coefficient is calculated using the following equation:

$$k = \frac{15(1-fe)(\epsilon)\ D}{r^2\ \ \tau'} \times 60\ \frac{\text{sec}}{\text{min}}$$

An average value for D/τ' is obtained using the rate data (Table 17) and the graph in Figure C-1. To determine D/τ', a value for the parameter A is needed. This is easily calculated:

$$A = \frac{(1-\epsilon)\rho s K_{B'}}{\epsilon} = \frac{(1-.45)(1.08)(480)}{.45} = 634$$

Table 32 is a listing of experimental data and calculated D/τ' results. D/τ' is calculated from:

$$D/\tau' = \frac{(\text{x-coord value})^2(1+A)r^2}{T}$$

Finally:

$$k = \frac{15\ (1-.29)}{(.025)^2}\ (.45)(1.19 \times 10^{-5})\ (60) = 5.5 \text{ min}^{-1}$$

TABLE 31

EXPERIMENTAL PARAMETERS FOR PREDICTING PDC CONCENTRATION HISTORY ON XAD-4 COLUMNS

Parameter	Column A	Column B
A'	.95 cm^2	.95 cm^2
BV	10.4 cc	23.9 cc
Ca (feed)	2370 mg/L	2350 mg/L
fi[a]	.36	.37
fs[b]	.34	.35
fe[c]	.30	.28
K_B	480 cc/g	480 cc/g
k	5.5 min^{-1}	5.5 min^{-1}
ℓ	10.9 cm	25.2 cm
R	2.79 cm/min	3.23 cm/min
R'	2.65 cc/min	3.07 cc/min
r (estimated)	.025 cm	.025 cm
Wads	3.84g	9.12g
ϵ[d]	.45 mL/mL	.45 mL/mL
ρs[d]	1.08 g/ML	1.08 g/mL
pore vol.[d]	.96 mL/g	.96 mL/g
s	21.5	42.9
T_{mL}	1825 t/s	4346 t/s

[a] $fi = \frac{\text{(pore vol.)(Wads)}}{\text{BV}}$

[b] $fs = \frac{\text{Wads}}{\text{(BV)}\,(\rho s)}$

[c] $fe = 1 - (fi + fs)$

[d] Reference 14

TABLE 32

CALCULATION OF D/τ' FROM THE RATE OF ADSORPTION OF 1,2-DICHLOROPROPANE BY XAD-4[a]

T (sec)	$\frac{Q}{Q\ sat}$	$\left[\frac{(D/\tau')\ T}{(1 + A)\ r^2}\right]^{1/2}$	D/τ' (cm^2/sec)[b]
780	.487	.168	1.44×10^{-5}
1200	.557	.200	1.32×10^{-5}
1620	.636	.238	1.39×10^{-5}
2100	.679	.263	1.31×10^{-5}
3000	.688	.268	$.95 \times 10^{-5}$
3960	.694	.272	$.74 \times 10^{-5}$

[a] Rate data from Table 17

[b] Ave. value is 1.19×10^{-5} cm^2/sec

Calculation of Breakthrough Curves

As described in Appendix C the theoretical performance of a fixed bed of adsorbent is calculated from parameters s and t. The experimental parameters required for such calculations are listed in Table 31.

1. PDC Adsorption by XAD-4 at 16 BV/hr - Column A

$$s = \frac{kl}{R} = \frac{(5.5)(10.9)}{2.79} = 21.5$$

$$t = \frac{k}{fi'}\left(T - \frac{lfe}{R}\right);\ fi' = fi + fs\rho sK_{B'}$$

Rearranging the above in terms of t/s and solving for T:

$$T = \frac{fi'l}{R}\left(\frac{t}{s} + \frac{fe}{fi'}\right)$$

$$\text{since } \frac{fe}{fi'} = \frac{.30}{.36 + (.34)(1.08)(480)} \approx 0$$

$$T = \frac{fi'l}{R}\left(\frac{t}{s}\right)$$

For correlation with experimental data already presented, T may be expressed in terms of volume (mL) rather than time

$$T = \frac{fi'l}{R} \times R'\left(\frac{t}{s}\right) =$$

$$\frac{[.36+(.34)(1.08)(480)]}{2.79}(10.9)(2.65)\frac{t}{s} = 1825\frac{t}{s}$$

Using Figure C-2, at a particular value of t/s (corresponding to a time T in mL), and at a given s (21.5 in this case), the concentration history λ can be determined. Graphs of the theoretical versus experimental breakthrough curves for PDC on a 10.4 mL BV column of Amberlite XAD-4 loaded at a flow of 16 BV/hr are shown in Figure 47. Agreement during the early stages of breakthrough is good. For example, this column is predicted to treat 1160 mL (111 BV) to 10% leakage and was found to treat 1240 mL (119 BV). Somewhat more detailed and accurate breakthrough data can be obtained using the published mass transfer tables [18,29,30].

2. PDC Adsorption by XAD-4 at 8 BV/hr - Column B

$$s = \frac{kl}{R} = \frac{(5.5)(25.2)}{3.23} = 42.9$$

$$T = \frac{fi'l}{R} \times R'\left(\frac{t}{s}\right) =$$

$$\frac{[.37+(.35)(1.08)(480)]}{3.23}(25.2)(3.07)\frac{t}{s} = 4346\frac{t}{s}$$

Again, data needed to plot the concentration history are obtained using Figure C-2. Graphs of the predicted and observed breakthrough curves for PDC on a 23.9 mL BV column of Amberlite XAD-4 loaded at a flow of 8 BV/hr are shown in Figure 47. This column is predicted to treat 3200 mL (134 BV) to 10% leakage and was found to treat 3360 mL (141 BV).

3. Nitroaromatic Adsorption on XAD-4 Columns

The performance model was also tested with multicomponent stream data. Attempts at modelling the column performance of each individual stream component (i.e. toluene, nitrobenzene, 2-nitrophenol, and 2,4-dinitrotoluene) resulted in poor agreement between predicted and observed column behavior. However, using cumulative component data for each test, satisfactory agreement between predicted and observed column performance was obtained. Because DNT contributed less than 5% to the total waste stream concentration and was never detected in column effluent (vide supra) it was excluded from all calculations. Thus, cumulative data (i.e. the summation of T, NB, and NPL results) for batch and rate studies were used to predict column performance (i.e. cumulative breakthrough data for T, NB, and NPL).

The experimental parameters for predicting nitroaromatic concentration history on two XAD-4 columns are listed in Table 33. Column A refers to the 8 BV/hr study while Column B refers to the 16 BV/hr study. The data needed to calculate the mass transfer coefficient are recorded in Table 34. Using batch data, an equilibrium constant of 720 cc/g is calculated; using rate data, a mass transfer coefficient of 12.2 min^{-1} is calculated. Application of these values to equations for calculating the performance of a fixed bed of adsorbent (Appendix C) results in the following values for the column performance parameters s and T: 92.5 and 2736 t/s (8 BV/hr); 48.7 and 2749 t/s (16 BV/hr). The concentration history is obtained for each column by using the graph in Figure C-2. Plots of the predicted and observed breakthrough curves for nitroaromatics loading on XAD-4 columns are shown in Figure 48. To 10% leakage, the 8 BV/hr column is predicted to treat 2200 mL (208 BV) and was found to treat 2100 mL (198 BV). Similarly the 16 BV/hr column is predicted to treat 2060 mL (194 BV) to 10% leakage and was found to treat 1950 mL (184 BV).

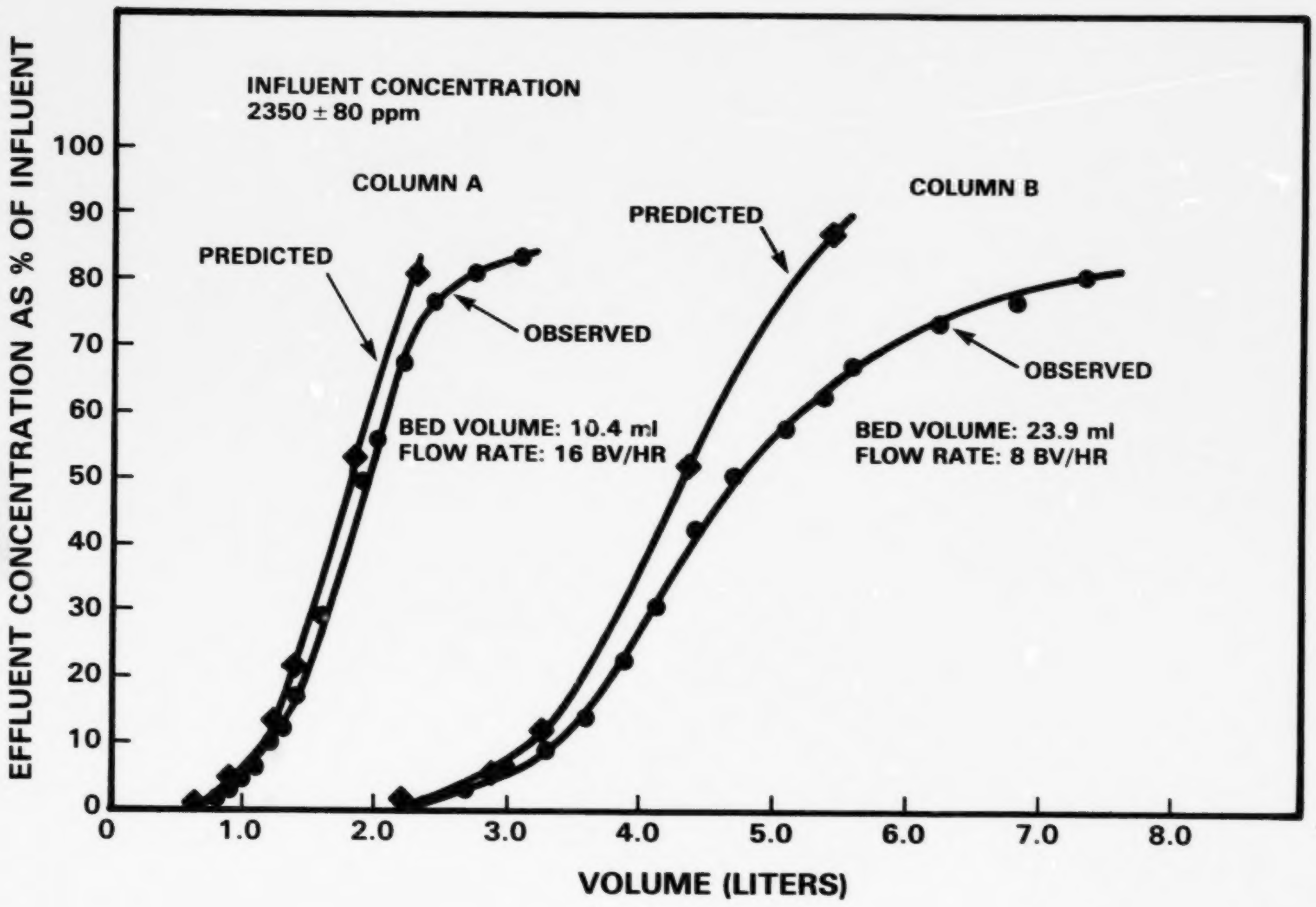


FIGURE 47. CORRELATION OF PREDICTED AND OBSERVED COLUMN ADSORPTION OF 1,2-DICHLOROPROPANE BY AMBERLITE XAD-4

TABLE 33

EXPERIMENTAL PARAMETERS FOR PREDICTING NITROAROMATIC CONCENTRATION HISTORY IN XAD-4 COLUMNS

Parameter	Column A	Column B
A'	.95 cm^2	.95 cm^2
BV	10.6 cc	10.6 cc
Ca (feed)[a]	1370 mg/L	1410 mg/L
fi	.35	.35
fs	.33	.33
fe	.32	.32
K_B[b]	720 cc/g	720 cc/g
k	12.2 min^{-1}	12.2 min^{-1}
ℓ	11.2 cm	11.2 cm
R	1.47 cm/min	2.81 cm/min
R'	1.40 cc/min	2.67 cc/min
r (estimated)	.025 cm	.025 cm
Wads	3.83g	3.80g
ϵ[c]	.45 mL/mL	.45 mL/mL
ρs[c]	1.08 g/mL	1.08 g/mL
pore vol.[c]	.96 mL/g	.96 mL/g
s	92.5	48.7
T_{mL}	2736 t/s	2749 t/s

[a] $Ca(feed) = Ca_T + Ca_{NB} + Ca_{NPL}$

[b] $$K_B = \frac{\sum Qsat\ (T,NB,NPL)}{\sum C_s\ (T,NB,NPL)}$$

[c] Reference 14

TABLE 34

CALCULATION OF D/τ' FROM THE RATE OF ADSORPTION OF NITROAROMATICS BY XAD-4[a]

T (sec)	$\frac{Q^{b}}{Q\ sat}$	$[\frac{(D/\tau')\ T}{(1 + A)\ r^2}]^{1/2}$	$D/\tau'(cm^2/sec)^{c}$
600	.474	.163	2.60×10^{-5}
900	.610	.225	3.36×10^{-5}
1530	.714	.283	3.12×10^{-5}
1860	.742	.300	2.89×10^{-5}
3300	.768	.318	1.83×10^{-5}

[a] Rate data from Table 23

[b] $\frac{\sum Q\ (T,NB,NPL)}{\sum Q\ sat\ (T,NB,NPL)}$

[c] Ave. value is 2.76×10^{-5} cm^2/sec

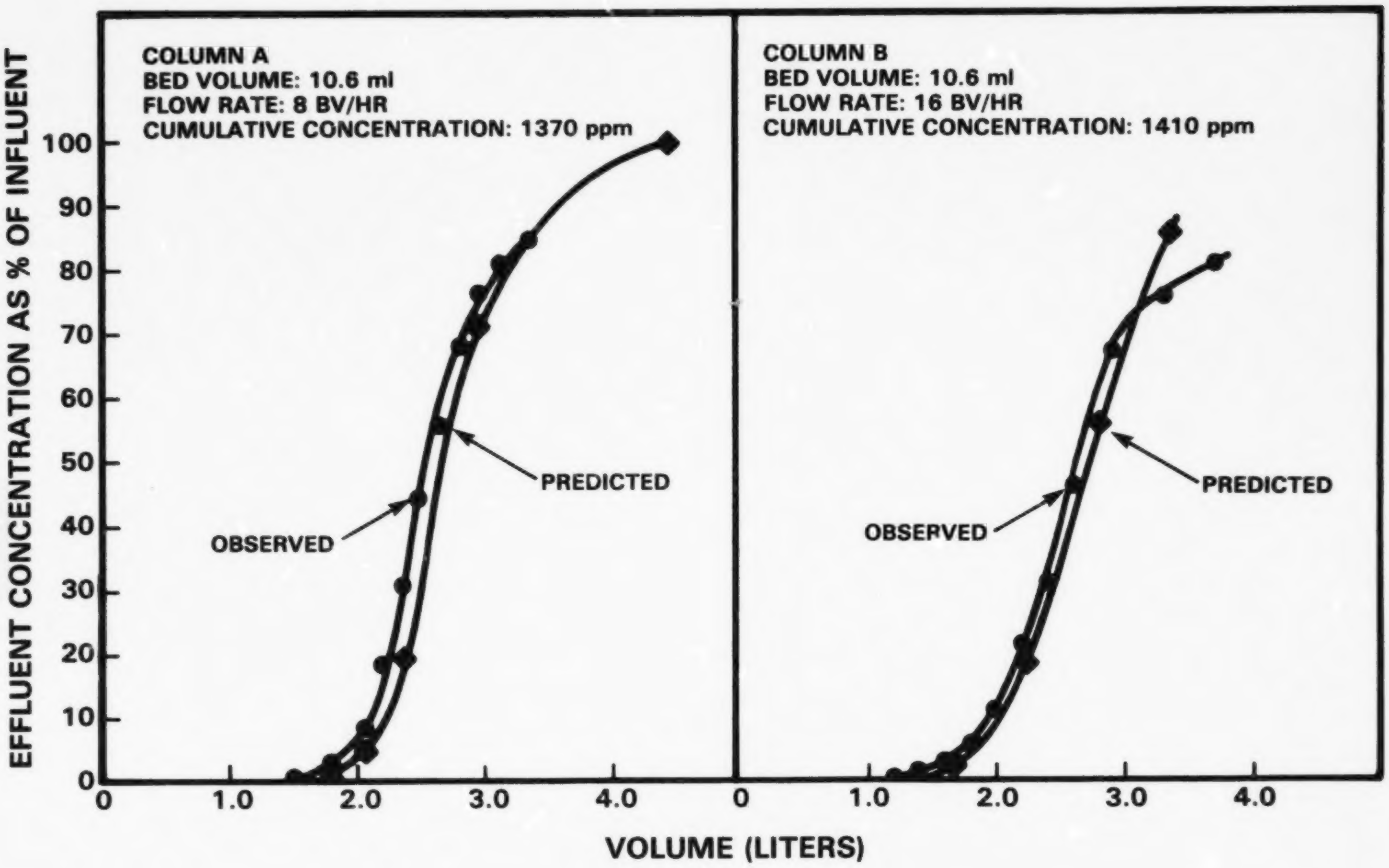


FIGURE 48. CORRELATION OF PREDICTED AND OBSERVED COLUMN ADSORPTION OF NITROAROMATICS BY AMBERLITE XAD-4

CORRELATION OF PREDICTED AND OBSERVED COLUMN PERFORMANCE

Comparisons of predicted and observed column performance for eight columns of Amberlite XAD-4 are listed in Table 35. Predicted values are usually within 10% of experimental values at 1% and 10% leakage. Considering the limited number of experimental parameters required and the simplicity of the calculations, this is very good agreement. The model adequately predicts column performance of XAD-4 in treatment of single and multicomponent waste streams.

Based on experimental results, the following physical parameters can be assumed for future calculations of XAD-4 column performance: $\rho s = 1.08$; $\epsilon = 0.45$; $fe = 0.32$; $fi = 0.34$; $fs = 0.33$. Thus, the only experimental studies required for purposes of predicting column performance of XAD-4 are batch/rate tests (i.e., to obtain data to calculate K_B and k). Reasonable estimates of these physical parameters are also required for predicting column performance of other synthetic adsorbents. Preliminary experimental evidence indicates that similar bed packing parameters (fe, fi, fs) can be used for Diaion HP-20. However, for the acrylic adsorbents, Amberlites XAD-7 and XAD-8, the parameters appear to be very different: $fi \approx fs \approx 0.22$ and $fe \approx 0.55$.

The performance model does not satisfactorily predict column behavior of the carbonaceous adsorbents. For example, in studies of adsorption of DNT by Ambersorb XE-340, batch tests yield a K_B of 770 cc/g and duplicate rate tests yield a k of 1.5 ± 0.4 min^{-1}. For a 90-95% correlation between predicted and observed column performance, a k of 5 ± 0.5 min^{-1} is required. The failure of the performance model in this application is believed to be due to the different pore structure (i.e. pore size and distribution) of carbonaceous adsorbents as compared to polymeric adsorbents [4].

ESTIMATION OF INITIAL COLUMN BREAKTHROUGH FROM BATCH DATA

Although column studies have demonstrated that batch data satisfactorily predict column saturation capacity, in normal column operation a loading cycle is terminated significantly before saturation is reached, usually at 1 to 10% leakage. For both single and multicomponent waste streams, a rough estimate of column performance can be made from batch data alone. For the multicomponent stream, again the components are summed and treated as a single component (vide supra). Based on data from fifteen column studies with four different waste streams at flows of 8 or 16 BV/hr (Table 36), the column capacity and volume treated to 1% and 10% leakage can be approximated as follows:

1. Capacity at 1% leakage = batch capacity X R_1

   or

$$\text{Volume treated to 1\% leakage} = \frac{\text{batch capacity X grams adsorbent}}{\text{influent concentration}} \text{ X } R_1$$

2. Capacity at 10% leakage = batch capacity X R_{10}

or

$$\text{Volume treated to 10\% leakage} = \frac{\text{batch capacity X grams adsorbent}}{\text{influent concentration}} \text{ X } R_{10}$$

where, for single component streams:

R_1 = .65 (at 8 BV/hr)
= .50 (at 16 BV/hr)
R_{10} = .80 (at 8 BV/hr)
= .70 (at 16 BV/hr)

and, for multicomponent streams:

R_1 = .55 (at 8 or 16 BV/hr)
R_{10} = .70 (at 8 or 16 BV/hr)

Thus, with a single measurement, the batch test, column capacity to 10% leakage can be roughly estimated to be 70% of the batch capacity.

TABLE 35

SUMMARY OF PREDICTED AND OBSERVED COLUMN PERFORMANCE OF AMBERLITE XAD-4

Adsorbate[a]	K_B (cc/gm)	k (min^{-1})	Column BV (mL)	Flow BV/hr	BV Treated to 1% BT		BV Treated to 10% BT	
					PRED	OBSV	PRED	OBSV
Nitrobenzene	760	5.0	11.0	16	113	137	163	181
Nitrobenzene	760	5.0	23.1	8	161	175	183	202
1,2-Dichloropropane	480	5.5	10.4	16	77	73	111	119
1,2-Dichloropropane	480	5.5	23.9	8	100	105	134	141
2,4-Dinitrotoluene	2500	10.5	11.4	24	398	389	548	490
2,4-Dinitrotoluene	2500	10.5	10.4	16	497	435	669	615
Nitroaromatics	720	12.2	10.6	16	142	124	194	184
Nitroaromatics	720	12.2	10.6	8	170	151	208	198

[a] See Tables 29 and 30 for concentrations.

TABLE 36

CORRELATION OF BATCH DATA AND INITIAL LEAKAGE IN COLUMN EXPERIMENTS

Adsorbate	Adsorbent	Flow (BV/hr)	R_1[a]	R_{10}[b]
Nitrobenzene	XAD-4	8	.70	.81
Nitrobenzene	HP-20	8	.73	.82
1,2-Dichloropropane	XAD-4	8	.61	.83
1,2-Dichloropropane	XAD-7	8	.53	.70
Nitroaromatics[c]	XAD-4	8	.54	.70
Nitroaromatics	HP-20	8	.60	.68
Nitroaromatics	XE-340	8	.45	.70
Nitrobenzene	XAD-4	16	.57	.71
Nitrobenzene	XAD-8	16	.41	.59
1,2-Dichloropropane	XAD-4	16	.46	.69
1,2-Dichloropropane	HP-20	16	.55	.73
2,4-Dinitrotoluene	XAD-4	16	.47	.66
2,4-Dinitrotoluene	XE-340	16	.49	.72
Nitroaromatics[c]	XAD-4	16	.50	.70
Nitroaromatics	HP-20	16	.58	.66
2,4-Dinitrotoluene	XAD-4	24	.45	.56

[a] $$R_1 = \frac{\text{(Capacity at 1\% Leakage)}}{\text{Batch Capacity}}$$

$$= \frac{\text{Volume treated to 1\% leakage x influent conc.}}{\text{Batch capacity x grams adsorbent}}$$

[b] $$R_{10} = \frac{\text{(Capacity at 10\% Leakage)}}{\text{Batch Capacity}}$$

$$= \frac{\text{Volume treated to 10\% leakage x influent conc.}}{\text{Batch capacity x grams adsorbent}}$$

[c] The nitroaromatics stream contains toluene, nitrobenzene, 2-nitrophenol, and 2,4-dinitrotoluene.

REFERENCES

1. I. H. Suffet and M. J. McGuire, Ed., Activated Carbon Adsorption of Organics from Aqueous Phase, Vol. 1, Ann Arbor Science Publishers, Ann Arbor (1980).

2. J. W. Neely and E. G. Isacoff, The Use of Carbonaceous Adsorbents for Treatment of Ground and Surface Waters, Marcel Dekker, Inc., New York (1982).

3. R. Kunin, "Porous Polymers as Adsorbents - A Review of Current Practice", Amber-hi-Lite No. 163, Rohm and Haas Company, Philadelphia (1980).

4. Ambersorb Carbonaceous Adsorbents, Publication IE-231, Rohm and Haas Company, Philadelphia (1980).

5. Summary Bulletin, Amberlite Polymeric Adsorbents, Publication IE-172, Rohm and Haas Company, Philadelphia (1979).

6. B. R. Kim, V. L. Snoeyink, and F. M. Saunders, "J. Water Poll. Cont. Fed.", 48, 120 (1976).

7. J. E. Millar, "J. Poly. Sci., Poly. Symp. 68", 167 (1980).

8. J. R. Perrich, Ed., Activated Carbon Adsorption for Wastewater Treatment, CRC Press, Inc., Boca Raton (1981).

9. R. A. Dobbs and J. M. Cohen, Carbon Adsorption Isotherms for Toxic Organics, EPA Report 600/8-80-023 (1980).

10. E. H. Crook, R. P. McDonnell, and J.T. McNulty, "Ind. Eng. Chem., Prod. Res. Dev.", 14, 113 (1975).

11. F. X. Pollio and R. Kunin, "Env. Sci. and Tech.", 1, 160 (1967).

12. H. E. Wise and P. D. Fahrenthold, "Env. Sci. and Tech.", 15, 1292 (1981).

13. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., Wiley-Interscience, New York (1980).

14. Technical Bulletin, Amberlite XAD-4, Publication IE-159-69, Rohm and Haas Company, Philadelphia (1978).

15. D. Ruggiero and R. Ausubel, Removal of Organic Contaminants from Drinking Water Supply at Glen Cove, NY, Phases 1 and 2, US EPA Cooperative Agreement CR-806355-01, US EPA, Cincinnati (1980, 1981).

16. J. K. Smith, R. J. Planchet, E. J. Westbrook, and F. J. Zak, Laboratory Studies of Priority Pollutant Treatability, EPA Report 600/2-81-129 (1981).

17. R. M. Carlyle, "Eff. and Water Treat. J.", (Feb. 1982).

18. F. G. Helfferich, Ion Exchange, McGraw-Hill, New York (1962).

19. T. Vermeulen and N. Hiester, "Ind. Eng. Chem.", 44, 636 (1952).

20. N. Hiester and T. Vermeulen, "Chem. Eng. Prog.", 48, 505 (1952).

21. R. Dedrick and R. Beckmann, "Chem. Eng. Prog., Symp. Ser. 74", 63, 68 (1967).

22. K. Hall, L. Eagleton, A. Acrivos, and T. Vermeulen, "Ind. and Eng. Chem. Fund.", 5, 212 (1966).

23. B. A. Bell and A. H. Molof, "Water Res.", 9, 857 (1975).

24. T. Keinath and W. Weber, J. Water Poll. Cont. Fed.", 40, 741 (1968).

25. W. Weber and M. Pirbazari, Effectiveness of Activated Carbon for Removal of Toxic and/or Carcinogenic Compounds from Water Supplies, EPA Report 600/S2-81-057 (1981).

26. W. Weber and M. Pirbazari, "J. Am. Water Works Assoc.", 203 (April, 1982).

27. B. van Vliet, W. Weber, and H. Hozumi, "Water Res.", 14, 1719 (1980).

28. B. van Vliet and W. Weber, "J. Water Poll. Cont. Fed.", 53, 1585 (1981).

29. S. Brinkley, Report 3172, US Dept. Int., US Bureau of Mines (1951).

30. A. Opler and N. Hiester, "Tables for Predicting the Performance of Fixed Bed Ion Exchange and Similar Mass Transfer Processes", SRI, Stanford (1954).

APPENDIX A

ABBREVIATIONS

BV - bed volumes
BV/hr - bed volumes per hour
cc - cubic centimeters (also cm^3)
cc/g - cubic centimeters per gram (also cm^3/g)
cm - centimeters
cm/min - centimeters per minute
GC - gas chromatograph
g - grams
gal - gallon
gpm/ft^3 - gallons per minute per cubic foot
L - liters
L/g-min - liters per gram per minute
m^2/g - square meters per gram
mg - milligrams
mg/g - milligrams per gram
mg/g-min - milligrams per gram per minute
mg/L - milligrams per liter
mL - millimeters
mL/min - milliliters per minute
mm - milliliters
μg - micrograms
μg/L - micrograms per liter
ppb - parts per billion (also μg/L)
ppm - parts per million (also mg/L)
rpm - revolutions per minute
sq in - square inches
CIS - cis-1,2-dichloroethylene
DNT - 2,4-dinitrotoluene
ETH - 1,1,1-trichloroethane
NB - nitrobenzene
NPL - 2-nitrophenol
PDC - 1,2-dichloropropane
TETRA - tetrachloroethylene
TRI - trichloroethylene

APPENDIX B

ADSORBENT CONDITIONING

1. Place the resin in a large beaker, add an equal volume of methanol (acetone), and allow the resin to soak for 30 minutes with occasional stirring.

2. Slurry the resin into an appropriately sized column and allow it to settle.

3. Pass deionized water upflow through the column at a rate sufficient to give 50% bed expansion.

4. Backwash with deionized water for 30 minutes or until complete classification of the bed is achieved (small beads at the top and large beads at the bottom). Allow the resin to settle.

5. Drain the water to 1 inch above the resin bed and pass 10 bed volumes of methanol (acetone) at 8 BV/hr downflow through the column.

6. Pass 20 bed volumes of deionized water downflow at a rate of 16 BV/hr.

7. Thoroughly drain the bed and blow 100% relative humidity air through the bed to remove as much excess water as possible.

8. Store the conditioned resin in a clean, tightly capped bottle.

APPENDIX C

THEORETICAL APPROACH TO COLUMN PERFORMANCE MODELING USING BATCH/RATE DATA

DETERMINATION OF THE LINEAR EQUILIBRIUM CONSTANT

Synthetic adsorbents exhibit a Langmuir-type equilibrium behavior which can be mathematically described as

$$\frac{q_a'}{q_{a\,\max}'} = \frac{\beta q_a}{1 + \beta q_a}$$

where q_a' is the concentration of a in the solid phase, q_a is the concentration of a in the liquid phase, $q_{a\,\max}'$ is the maximum value of q_a', and β is the Langmuir equilibrium constant.

Over a range of low concentrations, where $\beta q_a \ll 1$, the equilibrium relation is approximately linear and

$$q_a' = (\beta q_{a\,\max}')q_a = Kq_a$$

where K(cc/g) is the linear equilibrium constant. With the high concentrations of typical waste streams ($q_a > 100$ ppm), empirical factors can be applied to correct for non-linearity.

From the standpoint of performance, the equilibrium behavior of a "good" adsorbent would be described by a large value of K. Using data from typical isotherm experiments, the linear equilibrium constant can be determined from the equilibrium uptake, by a known amount of adsorbent, in a solution of known volume and concentration by:

$$K = \frac{1}{\rho_s(1-\epsilon)} \left[\frac{V_s\,(C_{so} - C_{s\infty})}{V_{ads}\,(C_{s\infty} - C_{ao})} - \epsilon\right]$$

All symbols used in column performance modeling are defined in Appendix D. Using batch data (regenerated batch equilibrium capacity) which is obtained for uptake from a solution of infinite volume and known concentration, the linear equilibrium constant K_B is determined by:

$$K_B = \frac{Q_{sat}}{C_s} \times 1000 \text{ cc/L}$$

If batch data must be obtained from a solution of limited volume, the equilibrium constant is modified and determined by:

$$K_B = \frac{V_s\,(C_{so} - C_{s\infty})}{W_{ads}\,(C_{s\infty})}$$

DETERMINATION OF THE MASS TRANSFER COEFFICIENT

The rate limiting step in achieving equilibrium in these systems can be any one or a combination of the following steps involved in the process:

1. Diffusion of material from the external fluid stream to the surface of the adsorbent bead (external mass transfer).
2. Diffusion of material from the surface of the adsorbent into the inner pore structure (internal mass transfer).
3. Sorption at the fluid-solid interface.
4. Diffusion of material through the solid phase (surface diffusion).

Experimental evidence indicates that for synthetic adsorbents, the rate limiting step is internal mass transfer. Sorption at the fluid-solid interface is extremely rapid and, in fact, local equilibrium can be assumed. Furthermore, for reasonable flow rates, the external mass transfer resistance is small compared to the internal resistance.

The mass transfer in a particular adsorbent can be described in terms of a mass transfer coefficient k (min^{-1}) as defined by:

$$\text{Mass Transfer} = k\,(C_a - q_a)$$

For the case of internal mass transfer limiting the rate:

$$k = \frac{15\,(1-fe)\epsilon}{r^2} \times \frac{D}{\tau'} \times \frac{60\ \text{sec}}{\text{min}}$$

The critical parameter that must be determined to estimate k is (D/τ'). This quantity is obtained experimentally from the rate of mass transfer into the adsorbent from a rapidly stirred solution of infinite volume (the rate test). Rate data are used in the form of fractional uptake (Q/Q_{sat}) as a function of time, T. In Figure C-1, these data lie on the y-coordinate. When the rate test is performed in a solution of infinite volume, the x-coordinate parameter

$$\left[\frac{\frac{D}{\tau'}\ T}{(1 + A)r^2}\right]^{1/2}$$

is determined using the 0% curve which denotes no change in solution concentration. If the test must be done in a solution of limited volume, one of the alternate curves which best corresponds to the final fractional uptake of adsorbate is used.

The parameter A is a function of the linear equilibrium constant. It appears in the calculation of the mass transfer coefficient because both diffusion and linear equilibrium are occurring simultaneously.

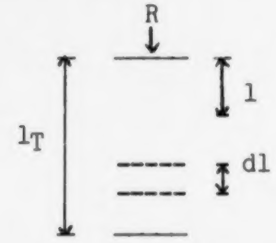
$$A = \frac{(1-\epsilon)\rho_s K}{\epsilon}$$

THEORETICAL BEHAVIOR OF A FIXED BED OF ADSORBENT

The performance of a fixed bed of adsorbent can be described mathematically, subject to the following assumptions:

1. uniform bed geometry
2. uniform feed (concentration, flow rate, temperature)
3. ideal plug flow outside the adsorbent with negligible axial dispersion (no flow within the adsorbent).

Under these conditions the governing equation can be obtained from a mass balance over an infinitesimal volume element A'dl over an infinitesimal time interval T.



$$RA'\left(C_a\Big|_{l} - C_a\Big|_{l+dl}\right) =$$

$$A'dl\left[fe\frac{\delta C_a}{\delta T} + fi\frac{\delta q_a}{\delta T} + fs\rho_s\frac{\delta q_a'}{\delta T}\right]$$

Assuming rapid, linear equilibrium such that $q_a' = Kq_a$, the equation simplifies to:

$$-R\left(\frac{\delta C_a}{\delta l}\right)_T = fe\left(\frac{\delta C_a}{\delta T}\right)_l + fi'\left(\frac{\delta q_a}{\delta T}\right)_l$$

where $fi' = fi + fs\rho_s K$

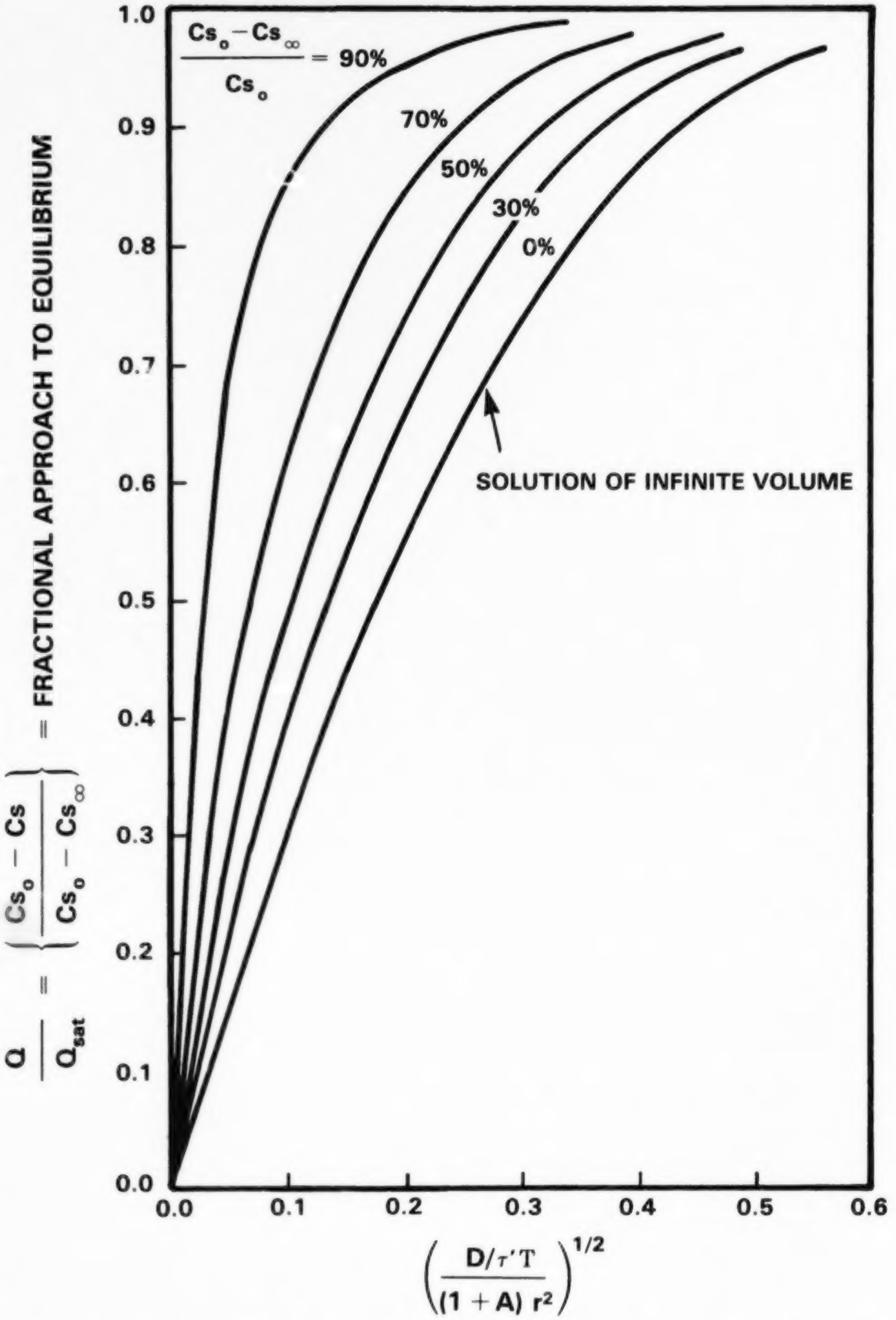


FIGURE C-1. SIMULTANEOUS DIFFUSION AND LINEAR ADSORPTION INTO A POROUS SPHERE

Letting t' = T-lfe/R and assuming the transfer rate is proportional to both a constant mass transfer coefficient (k) and the difference in average concentrations inside and outside the adsorbent, we obtain

$$-R\left(\frac{\delta C_a}{\delta l}\right)_{t'} = fi'\left(\frac{\delta q_a}{\delta t'}\right)_l = k(C_a - q_a)$$

This is the governing partial differential equation with the following boundary conditions:

$C_a = C_{a\ feed}$ for $T \geq 0$ at $l = 0$
$q_a = q_{ao}$ at l for $t' \leq 0$

It can be transformed into conventional dimensionless form to utilize the published solutions for fixed beds,[18,20]

$$-\left(\frac{\delta\lambda}{\delta s}\right)_t = \left(\frac{\delta\omega}{\delta t}\right)_s = \lambda(1-\omega) - r'\omega(1-\lambda)$$

where $\lambda = 1$ at $s = 0$; $\omega = 0$ at $t = 0$

using the transformations:

$$\lambda = \frac{C_a - C_{ao}}{C_{a\ feed} - C_{ao}}$$

$$\omega = \frac{q_a - C_{ao}}{C_{a\ feed} - C_{ao}}$$

$$r' = 1$$

$$s = \frac{kl}{R}$$

$$t = \frac{kt'}{fi'} = \frac{k}{fi'}\left(T - \frac{lfe}{R}\right)$$

λ is the solution function giving the concentration history. s is the column-capacity parameter. t is the solution-capacity parameter.

t/s is the throughput parameter. The generalized dimensionless solutions to these equations are [18,20,30]

$$\lambda = 1 - \int_0^s e^{(-t-z)} I_0(2\sqrt{tz})\,dz$$

$$\omega = \int_0^t e^{(-s-z)} I_0(2\sqrt{sz})\,dz$$

where I_0 is a modified Bessel function of the first kind. Helfferich [18] and others [29,30] present numerical solutions to the integrals in these equations for a wide range of t and s. The results are presented more conveniently in Figure C-2 and can be used to predict effluent concentration ($C_{a\ feed}$) for any value of time (T) given the following parameters:

1. Operating variables: $C_{a\ feed}$ (influent concentration)
   R (linear flow rate)
2. Physical parameters: fe, fi, fs (bed packing parameters)
   ρs (adsorbent density)
   ϵ (adsorbent porosity)
3. Equilibrium parameter: K_B
4. Mass transfer parameter: k

In characterizing the performance of a column, the adsorbent's physical parameters can be measured or simply estimated. After the completion of a representative number of column experiments using the various adsorbents available, a table of appropriate physical parameters can be included as part of column performance prediction methodology. The equilibrium and mass transfer parameters are determined from the batch/rate test as previously described.

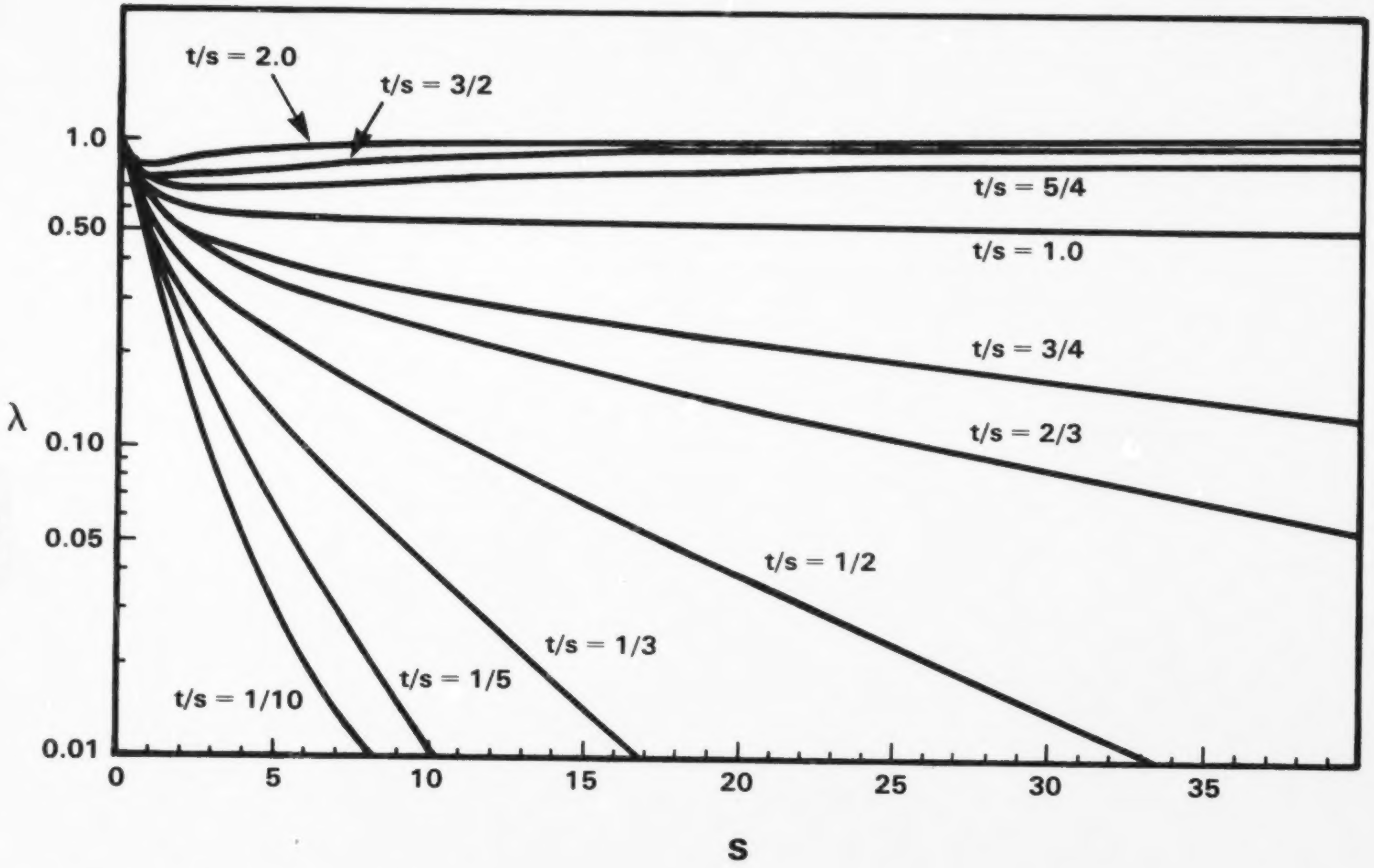


FIGURE C-2. GENERALIZED DIMENSIONLESS SOLUTIONS FOR HEAT TRANSFER AND OTHER MASS TRANSFER PROCESSES

APPENDIX D

SYMBOLS USED IN COLUMN PERFORMANCE MODELING

A' = bed cross sectional area (cm^2)
BV = bed volume of classified adsorbent (mL)
C_a = concentration of a in external channels - average (mg/L)
$C_{a\ feed}$ = feed or influent concentration (mg/L)
C_{ao} = initial C_a, prior to adsorbate exposure (mg/L)
C_a = C_a at equilibrium (mg/L)
C_s = solution concentration (mg/L)
C_{so} = initial solution concentration (mg/L)
$C_{s\infty}$ = solution concentration at equilibrium (mg/L)
D = diffusion coefficient
fe = external void fraction (bed void fraction)
fi = internal void fraction (bead void fraction)
fs = solid fraction
K = linear equilibrium constant (cc/g)
K_B = batch test linear equilibrium constant (cc/g)
$K_{B'}$ = modified batch test linear equilibrium constant (cc/g)
k = mass transfer coefficient (min^{-1})
l_T = total bed length (cm)
l = distance from top of bed (cm)
q_a = concentration of a in adsorbent pores - average (mg/L)
q_a' = concentration of a in solid phase (mg/L)
$q_{a\ max}'$ = q_a' as $q_a \longrightarrow \infty$ (mg/g)
Q = adsorbent capacity (mg/g)
Q_{sat} = adsorbent saturation capacity (mg/g)
R = flow rate into bed per unit cross-sectional area (cm/min)
R' = flow rate into bed (cc/min)
r = radius of adsorbent bead - average (cm)
s = column-capacity parameter
T = time (sec)
t = solution-capacity parameter
t/s = column throughput parameter

V_s = solution volume (mL)
V_{ads} = adsorbent volume (mL)
W_{ads} = adsorbent weight (g)
β = Langmuir equilibrium constant
ϵ = absolute adsorbent porosity (mL pore/mL adsorbent)
ρ_s = adsorbent skeletal density (g/mL)
τ' = tortuosity

APPENDIX E

GLEN COVE PILOT PLANT DATA

The following Tables and Figures have been reproduced from Reference 2, Chapter 6, with the authors' permission. The data were obtained during an EPA funded pilot plant study (U.S.E.P.A. No. CR 806355-01) investigating treatment methods for Glen Cove City groundwater contaminated by chlorinated organics.

TABLE E-1

GLEN COVE ADSORPTION SUMMARY

Column	Adsorbent	Cycle Number	Flow Rate	Compound[a]	Bed Volumes to 10% Leakage (Leakage ppb)	Days
1	ICI Carbon	1	2 gpm/ft^3	cis	15,000 (4)	40
1	ICI Carbon	1	2 gpm/ft^3	tri	25,700 (17)	67
1	ICI Carbon	1	2 gpm/ft^3	tetra	35,300 (6)	92
			<----Steam Regeneration---->			
1	ICI Carbon	2	2 gpm/ft^3	cis	5,000 (4)	13
1	ICI Carbon	2	2 gpm/ft^3	tri	14,200 (15)	37
1	ICI Carbon	2	2 gpm/ft^3	tetra	>35,300 (9)	>92
2	Calgon Carbon	1	2 gpm/ft^3	cis	17,300 (4)	45
2	Calgon Carbon	1	2 gpm/ft^3	tri	38,400 (17)	100
2	Calgon Carbon	1	2 gpm/ft^3	tetra	>49,000 (6)	130
			<----Steam Regeneration---->			
2	Calgon Carbon	2	2 gpm/ft^3	cis	3,000	8
2	Calgon Carbon	2	2 gpm/ft^3	tri	17,000 (15)	44
2	Calgon Carbon	2	2 gpm/ft^3	tetra	>21,000 (12)	>55
3	Ambersorb XE-340	1	4 gpm/ft^3	cis	27,000 (5)	35
3	Ambersorb XE-340	1	4 gpm/ft^3	tri	105,000 (17)	137
3	Ambersorb XE-340	1	4 gpm/ft^3	tetra	121,000 (7)	158
			<----Steam Regeneration---->			
3	Ambersorb XE-340	2	4 gpm/ft^3	cis	38,400 (7)	50
3	Ambersorb XE-340	2	4 gpm/ft^3	tri	<1 ppb after 46,000 (13)	>60[b]
3	Ambersorb XE-340	2	4 gpm/ft^3	tetra	<1 ppb after 46,000 (17)	>60[b]

CONTINUED

TABLE E-1 (CONTINUED)

GLEN COVE ADSORPTION SUMMARY

Column	Adsorbent	Cycle Number	Flow Rate	Compound[a]		Bed Volumes to 10% Leakage (Leakage ppb)	Days
4	Ambersorb XE-340	1	4 gpm/ft^3	cis		31,000 (7)	40
4	Ambersorb XE-340	1	4 gpm/ft^3	tri		69,000 (13)	90
4	Ambersorb XE-340	1	4 gpm/ft^3	tetra		>77,000 (7)	>100
5	Ambersorb XE-340	1	2 gpm/ft^3	cis		40,000 (4)	104
5	Ambersorb XE-340	1	2 gpm/ft^3	tri		80,000 (20)	208
5	Ambersorb XE-340	1	2 gpm/ft^3	tetra		83,000 (6)	216
<----Steam Regeneration---->							
5	Ambersorb XE-340	2	2 gpm/ft^3	cis		23,000 (6)	60
5	Ambersorb XE-340	2	2 gpm/ft^3	tri	4.1 ppb after	23,000 (17)	>60
5	Ambersorb XE-340	2	2 gpm/ft^3	tetra	1.4 ppb after	23,000 (9)	>60
<-------This Column was stopped prematurely and then Steam Regenerated---->							
5	Ambersorb XE-340	3	4 gpm/ft^3	cis		15,000 (4)	20
5	Ambersorb XE-340	3	4 gpm/ft^3	tri		69,000 (17)	90
5	Ambersorb XE-340	3	4 gpm/ft^3	tetra		77,000 (6)	100
<----Steam Regeneration---->							
5	Ambersorb XE-340	4	4 gpm/ft^3	cis		28,000 (5)	36
5	Ambersorb XE-340	4	4 gpm/ft^3	tri		64,000 (16)	83
5	Ambersorb XE-340	4	4 gpm/ft^3	tetra		73,000 (11)	95

[a] cis = cis-1,2-dichloroethylene
tri = trichloroethylene
tetra = tetrachloroethylene

[b] Still in progress

FIGURE E-1

COLUMN #1 — 4gpm/ft³ — CIS 1,2 DICHLOROETHYLENE LEAKAGE

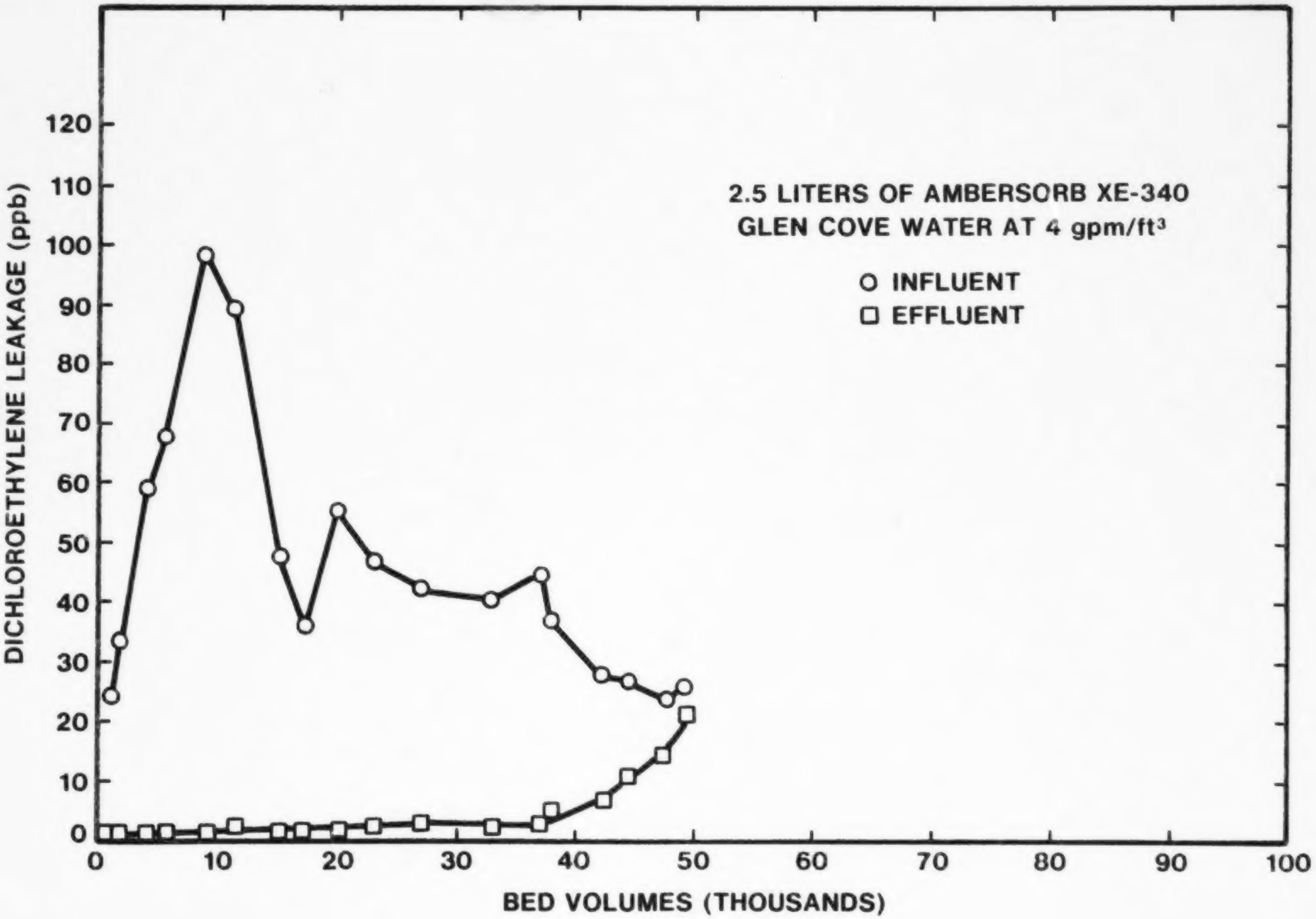


FIGURE E-2

COLUMN #1 — 4gpm/ft³ — TRICHLOROETHYLENE LEAKAGE

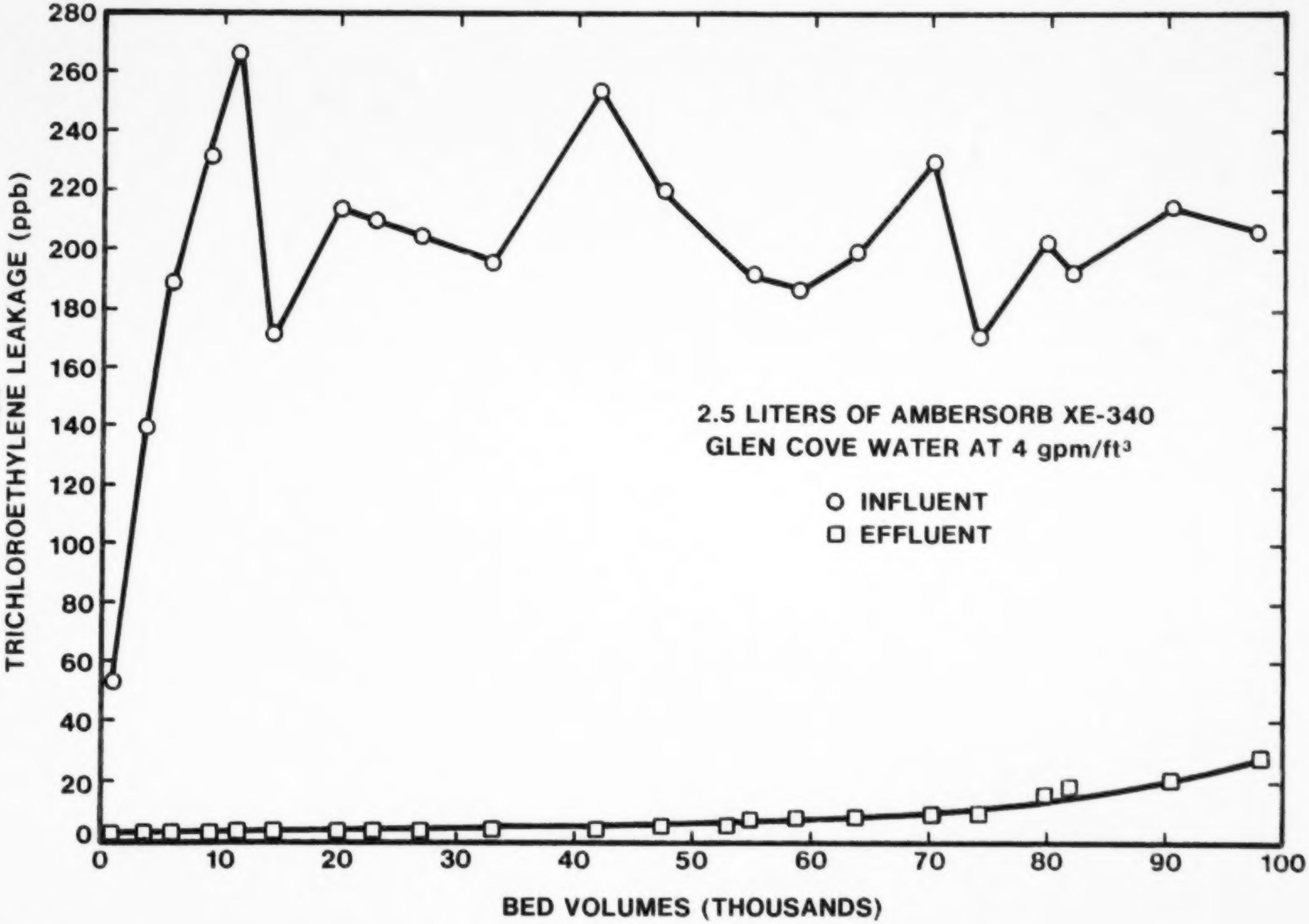


FIGURE E-3

COLUMN #1 — 4gpm/ft³ — TETRACHLOROETHYLENE